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A Bromo(boryloxy) Silylene and its Heavier Analogues

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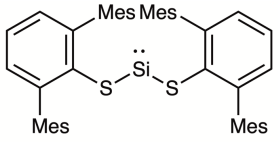
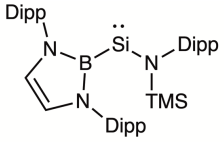
A N-heterocyclic boryloxy ligand equipped with bulky diazaboryl *N*-substituents is used to synthesize divalent and dicoordinate group 14 compounds which represent the first examples of acyclic halo(boryloxy) tetrylenes. The bromo(boryloxy) silylene reacts swiftly with benzophenone to a siloxindane.

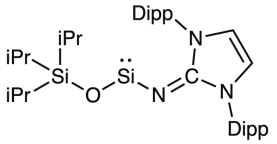
Since West reported the first cyclic diamino silylenes in 1994,[1,2] several other cyclic systems like alkylamino[3] and dialkyl[4] silylenes were published and their intriguing reaction behaviour was widely explored during the last years.[5–11] For a long time stable silylenes with a di-coordinate silicon centre were restricted to cyclic compounds with bulky substituents, and acyclic silylenes were considered as too reactive for isolation.[12] This changed in 2012 when the first two examples of stable acyclic congeners with two-coordinate silicon were isolated – a bis(arylthio) silylene (**I**) and a boryl(amino) silylene (**II**).[13,14] The high reactivity of one of these compounds fulfilled expectations – e. g. the latter reacts swiftly with dihydrogen at room temperature. Due to their potential in modern synthetic chemistry, the study of acyclic silylenes is still an emerging topic where the variation of the substituents is most important to achieve different electronic properties, and thus reaction behaviour.[12] Recently, the group of Inoue reported that an imino(silyl) silylene reacts with CO_2 to form an acyclic silanone[15] which can be isolated as a solid but gets converted to an imino(siloxy) silylene (**III**) in solution. Aldridge *et. al.* reported an acyclic silylene (**IV**) bearing two $(HCNDipp)_2BO$ (**{B}**O) substituents which marks the first acyclic silylene coordinated by only two oxygen atoms.[16] These two examples indicate that not only nitrogen, but also oxygen-based substituents are suitable for the isolation of acyclic silylenes.



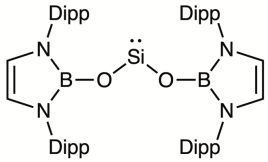
I, Power 2012



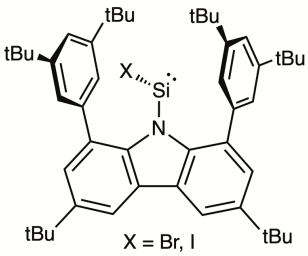
II, Aldridge, Jones 2012



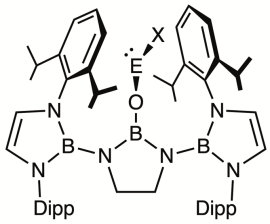
III, Inoue 2017



IV, Aldridge 2019



V, Hinz 2020



E = Si, X = Br
E = Ge, X = Cl
E = Sn, X = Cl

This work

For tri-coordinate silicon compounds, which can be realized by intramolecular coordination of a monoanionic but bidentate ligand, or by an external Lewis base, the bulk of the substituents is less crucial for isolation. In this context, from a formal point of view, the first acyclic silylene with one monoatomic chloro substituent was isolated using an monoanionic amidinate ligand by Roesky in 2006[17] and even a dichloro silylene can be isolated as a carbene adduct.[18]

The first halo silylene (**V**) with a strictly di-cordinated silicon centre was isolated by Hinz in 2022, utilizing a bulky carbazolyl substituent to stabilize the SiX (X = Br, I) moiety.[19] This halo(amino) silylene shows some unique properties and served

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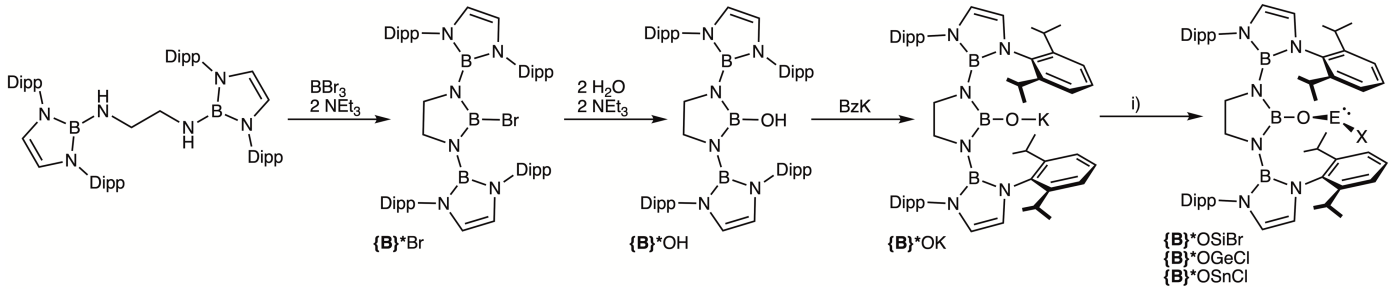
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 1: Synthesis of halo(boryloxy) tetrylenes. i) for E = Si: 1. $SiBr_4$; 2. $[(MesNacNac)Mg]_2$; for E = Ge: $[GeCl_2(1,4\text{-dioxane})]$; for E = Sn: $SnCl_2$.

as the precursor for the first close to monosubstituted silicon(II) cation.

Inspired by Hinz' base free halo silylene and Aldridge's boryloxy silylene we decided to synthesize a new boryloxy substituent and use it to prepare a base free halo silylene and its heavier analogues.

For the synthesis of the new protio-ligand **{B}***OH, the corresponding boron bromide **{B}***Br was synthesized using $[(HCNDipp)_2BNHCH_2]_2$[20] (Dipp = 2,6-di*iso*propylphenyl) and BBr_3 in the presence of two equivalents of triethylamine, with heating to 60 °C (see Scheme 1). In this step the reaction conditions were found to be critical to avoid the formation of several by-products which were never identified. Nevertheless, **{B}***Br was fully characterized and will be discussed in more detail in the context of another study. Note that the diamine $[(HCNDipp)_2BNHCH_2]_2$ has previously been used to stabilize subvalent group 14 compounds[20,21] and further that the diazaboryl substituent $(HCNDipp)_2B$ (**{B}**) has broadly served as a substituent in sub-valent main group chemistry.[22–24] For the current work we converted {**B}***Br into the boronic acid **{B}***OH by stirring **{B}***Br in toluene with triethylamine and water. Isolated **{B}***OH was subsequently deprotonated with benzyl potassium in *n*-hexane or toluene, with brief ultra-sonification, to give **{B}***OK in quantitative yield. In the solid-state structure, obtained from X-ray experiments with single crystals of the benzene solvate, the potassium atom shows M···arene interactions to the Dipp groups as well as to a capping benzene molecule, realizing a higher coordination number (see Figure S44). The oxygen atom shows a linear coordination mode (B–O–K 180.0°) and a comparably short B–O bond of 1.291 Å ($K\cdots centroid_{benzene}$ = 3.68 Å), which is comparable to the B=O double bond of Aldridge's anionic oxoborane (1.273(8) Å). In that case the use of [2.2.2]Cryptand was necessary to avoid the formation of dimeric $(\{B\}OK)_2$ in the solid state, and to access a separated ion pair.[25]

The metathesis reactions of **{B}***OK with $SiHCl_3$, $SiCl_4$ or $SiBr_4$ in toluene lead to a swift conversion to **{B}***$OSiHCl_2$ (^{29}Si: 38.7 ppm), **{B}***$OSiCl_3$ (^{29}Si: 48.3 ppm) and **{B}***$OSiBr_3$ (^{29}Si: 89.0 ppm), respectively. All compounds were fully characterized and studied by X-ray diffraction experiments (see Figure S45 – S47). While the two flanking diazaboryl rings of **{B}***OH and **{B}***OK are only slightly twisted out of the central ring plane (23.5°, 41.1° for **{B}***OH and 23.16° for **{B}***OK), the orientation of the diazaboryl substituent seems to be able to rotate around the exocyclic N–B bond and realize angles between those rings of up to 78° in the case of **{B}***$OSiBr_3$. This indicates that the system is quite flexible which allows π-interaction of the arene systems to an O-bonded fragment, and at the same time steric shielding perpendicular to the plane of ring system and the B–O bond.

We investigated the reactivity of these silicon(IV) compounds towards alkali metals (Li, Na, K), but we did not observe the formation of a new, well-defined product. At the same time the magnesium(I) reducing agent $[\{(MesNacnac)Mg\}_2]$[26] (MesNacnac = $[HC(MeCNMes)_2]^-$, Mes = mesityl) did not react with **{B}***$OSiHCl_2$ or **{B}***$OSiCl_3$. In reactions with **{B}***$OSiBr_3$ we observed the consumption of one equivalent of the dimagnesium(I) compound after stirring at room temperature, which is in line with a reduction from Si(IV) to Si(II). This was accompanied by the formation of two equivalents of (MesNacnac)MgBr. After extracting with *n*-hexane, filtration and drying under vacuum a yellow oil was isolated which slowly solidifies. In ^{29}Si NMR spectroscopic experiments we observe a sharp signal at 82.8 ppm for this compound which is a plausible shift for the target bromo(boryloxy) silylene, lying in between Hinz' dicoordinate bromo(amino) silylene (129.2 ppm),[19] Aldridge's bisboryloxy silylene (35.5 ppm)[16] and Inoue's iminato(siloxy) silylene (58.9 ppm)[15]. Attempts to grow single crystals suitable for X-ray studies failed due to the tendencies of the compounds to precipitate as an amorphous powder or remain as an oil.

The heavier group 14 analogues **{B}***OGeCl and **{B}***OSnCl are accessible from the metathesis reactions of **{B}***OK with $[GeCl_2(1,4\text{-dioxane})]$ and $SnCl_2$, respectively. The tetrylenes can

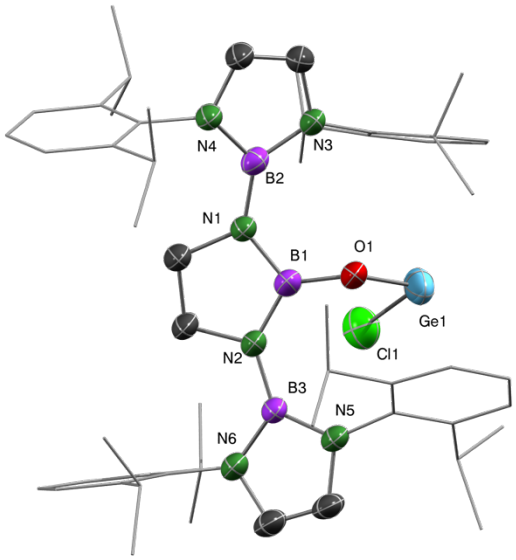


Figure 1: Molecular structure of **{B}***OGeCl in the solid state. Hydrogen atoms are omitted, and Dipp groups are shown as wire frame for clarity. Ellipsoids are presented at 50% probability level. Only one of the four molecules present in the unit cell is shown.

be separated from inorganic by-products and extracted with *n*-hexane. Unfortunately, we observe that the sensitive compounds tend to co-crystalize with **{B}***OH which is formed due to contact with traces of moisture. With that, recrystallization could not be used for further purification. Nevertheless, carefully performed reactions deliver products in sufficient purity for analyses. In ^{119}Sn nmr experiments the Stannylene exhibits one signal with a chemical shift of –181 ppm. This value is close to other congeners with oxygen-based substituents like Aldridge's bisboryloxy stannylene ([**{B}**O]$_2$Sn, –109.0 ppm)[16] or [{(Me$_3$Si)$_2$CH}$_2$BO]$_2$Sn (–186 ppm)[27] while other acyclic stannylenes exhibit quite high ^{119}Sn nmr shifts.[9,14,28,29]

Single crystals of **{B}***OGeCl and **{B}***OSnCl were used for X-ray diffraction studies and to determine the solid-state structures of the germylene and the stannylene. We note that **{B}***OGeCl and **{B}***OSnCl do not crystallize very reproduceable and it took a few attempts to obtain single crystals of sufficient quality. Our final measurement of the solid-state structure of **{B}***OGeCl shows four germylene molecules in the asymmetric unit together with four benzene molecules (see Figure S48). In the case of the tin congener, we obtained single crystals from *n*-hexane with two independent molecules in the asymmetric unit and one solvent molecule embedded (see Figure S49). Considering the B–O–E angles (Ge: 130.2(3)°, 131.3(3)°, 132.6(3)°, 133.4(3)°; Sn: 125.2(2), 130.9(2)°, 133.1(2)°), the EX moieties are not within the plane of the heterocyclic NB(O)N unit. The B–O–E–Cl (E = Ge, Sn) arms are quite flexible which is not only shown by the variation of the just mentioned B–O–E angle but also by different orientation of the O–E–X unit with respect to the (NCH$_2$)$_2$B ring, occurring in variable angles between the planes of N–B–N and O–E–X (Ge: 62.3°, 66.7°, 68.3°, 68.9°; Sn: 54.1°, 61.0°, 72.0°). This is in line with a low rotational barrier around the O–E bond as expected for such acyclic systems.

We further investigated **{B}***OSiBr with theoretical methods (PBE1PBE/def2TZVP/GD3BJ) and found the molecule to be stable on the energy hypersurface and in a similar structural confirmation as its heavier analogues. While the HOMO and HOMO–1 are ligand centred, the HOMO–2 represents a lone pair like orbital with an energy of –6.49 eV with some electron distribution over the bromo substituent (see Figure 2). The LUMO of the molecule is a predominantly Si centred p_z shape orbital with small distribution over the O–Si–Br part and exhibits an energy of –1.45 eV. This results in an energy gap between these frontier orbitals of 5.04 eV, which is significantly smaller than the reported value for Aldridge's bisboryloxy silylene (**{B}**O)$_2$Si (5.45 eV, same level of theory).[16]

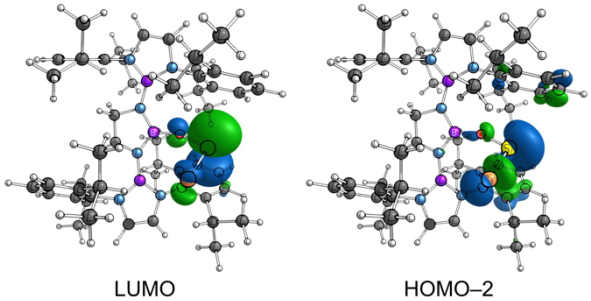
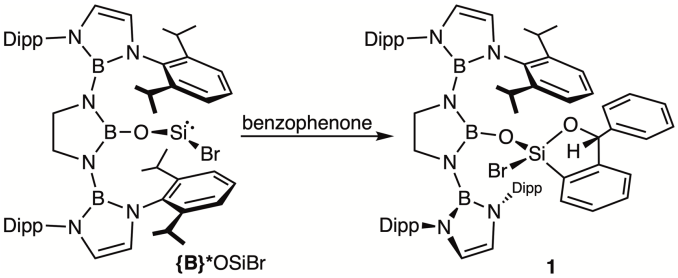


Figure 2: Frontier orbitals of **{B}***OSiBr derived from computational studies (PBE1PBE/def2TZVP/GD3BJ, isosurface of 0.05 $a_0^{-3/2}$).

In a recent study Hinz and co-worker showed that the bromo(amino) silylene **V** reacts smoothly with ethylene, acetylene, *tert*-butyl phosphaacetylene, 1,3-dibromobutane and dimethyl butadiene.[30] Together with Hinz' first report where it was shown that **V** can be converted to a silicon(II) cation by halide abstraction,[19] these are the only studies detailing the reactivity of dicoordinate halo silylenes. The reactivity of this rather new generation of silylenes is barely explored and it is not clear how the extreme bulk of the carbazolyl, which was necessary to isolate the silylene, prevents or affects reactions towards bigger substrates.

To evaluate the reactivity of **{B}***OSiBr towards electrophilic organic substrates, and convert the silylene into a new compound, we decided to study its reaction with benzophenone (see Scheme 2). For the more established cyclic silylenes the reactivity with ketones and especially benzophenone has already been investigated by several



Scheme 2: **{B}***OSiBr reacts with benzophenone to the siloxindane **1**.

groups.[31–33] In those reports the reactions are described to proceed *via* a [4+1] cycloaddition and dearomatization of one phenyl ring. Most of the silylenes subsequently undergo a 1,3-hydrogen shift and rearomatization to form a siloxaindane.[31,33–

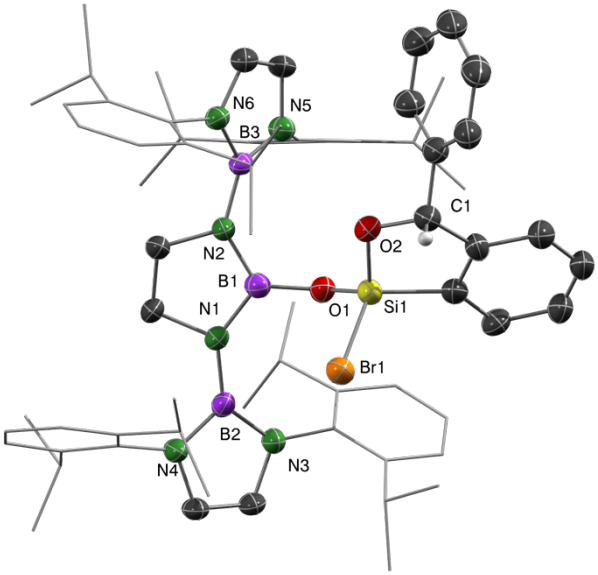


Figure 3: Solid state structure of **1** derived from X-ray diffraction experiments. For clarity Dipp groups are shown in a wireframe model and all H atoms except the C1 bound are omitted. All other atoms are shown with 50 % thermal ellipsoids.

[35] In our case the reaction of **{B}***OSiBr with benzophenone readily lead to the formation of the corresponding siloxaindane **1**, which was isolated in good yields (87 %) and was structurally characterized (see Figure 3). Note that there are two centres of chirality in **1** which are the former carbonyl atom and the silicon atom. Since we only observe the formation of one isomer with NMR spectroscopy and X-ray experiments, we assume a diastereoselective reaction pathway.

In summary, we present the new and very bulky boryloxy substituent **{B}***O which was used to synthesize a selection of halo(boryloxy) tetrylenes – a new class of compounds. The chloro(boryloxy) germylene and stannylene were structurally characterized, For the silylene **{B}***OSiBr we provide evidence that the bulky substituent allows the isolation of the strictly dicoordinate silicon compound. This is despite the steric profile of the ligand allowing reaction with benzophenone in a similar matter as is known for smaller, cyclic silylenes.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare.

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