An *N*-Heterocyclic Boryloxy Ligand Isoelectronic with *N*-Heterocyclic Imines: Access to an Acyclic Dioxysilylene and its Heavier Congeners

Ying Kai Loh,[†] Lu Ying,[†] M. Ángeles Fuentes, Dinh Cao Huan Do, and Simon Aldridge*

Abstract: We introduce a new type of strongly donating *N*-heterocyclic boryloxy (NHBO) ligand, [(HCDippN)₂BO]⁻, which is isoelectronic with the well-known *N*-heterocyclic iminato (NHI) donor class. This 1,3,2-diazaborole functionalized oxy ligand can be employed to stabilize the first acyclic two-coordinate dioxysilylene and its Ge, Sn and Pb congeners, thereby presenting the first complete series of heavier group 14 dioxycarbene analogues. All four compounds have been characterized by X-ray crystallography and Density Functional Theory (DFT), enabling analysis of periodic trends: the potential for the [(HCDippN)₂BO]⁻ ligand to subtly vary its electronic donor capabilities is revealed via snapshots revealing gradual evolution of arene π-coordination on going from Si to Pb.

Anionic oxygen-based ligands constitute a family of donors prevalent in the coordination chemistry of harder metal centres.[1] Among the most common are alkoxy (RO⁻) ligands, which stand out in having only one pendant substituent, thereby giving them the potential to donate 2σ+4π electrons to a metal centre – the maximum for any η¹ ligand system. The single substituent, however, offers only limited steric protection at the metal centre, meaning that O-bridged oligomeric structures are commonly encountered.[1b] This tendency towards aggregation is problematic for applications which involve low coordinate metal centres, for example ambiphilic main group species (such as carbenes and their heavier group 14 analogues) of interest in small molecule activation chemistry.[2]

An approach used to counter this problem exploits aryloxy (ArO⁻) ligands featuring bulky *ortho* substituents, thereby extending steric protection towards the metal centre. Thus, monomeric species of the type (ArO)₂E (E = Ge, Sn, Pb) have been reported by Lappert and by Power using this approach.[1c-e] That said, further chemistry with these systems typically involves the ArO⁻ unit acting as a leaving group (cf. *p*Ka of phenol = ~9), and being substituted by a stronger donor.[1f] A potential strategy to circumvent this problem is to replace the O-bound aryl substituent with a functional group based on a more electro-positive element such as boron (e.g. by employing boryloxy ligands, R₂BO⁻). A small number of ligands of this type have been reported, although for R = alkyl or aryl these are typically considered as *electron-deficient* alkoxide variants: the formally empty *p*-orbital at boron renders the R₂BO⁻ system a weak π donor.[3] Applications in main group chemistry are thus rare (limited primarily to groups 1, 2 and 13 complexes),[3b-d] although very recently Sarazin and co-workers isolated monomeric

species of the type (R₂BO)₂E (E = Sn, Pb, Ba) by employing the bulky (Me₃Si)₂HC group to inhibit dimerization.[3e-f]

With a view to targeting an isolable dioxy*silylene*, we saw a need for more strongly π donating boryloxy ligands which would potentially lead to a wide HOMO-LUMO gap on the basis of LUMO destabilization (O-to-Si π donation) *and* HOMO stabilization (high electronegativity of oxygen). A potential strategy appeared to us to revolve around the use of the diazaborolyl group (HCDippN)₂B⁻ as the O-bound substituent, which is known to be very sterically bulky, and only weakly π accepting due to the presence of amino substituents α to boron.[4]
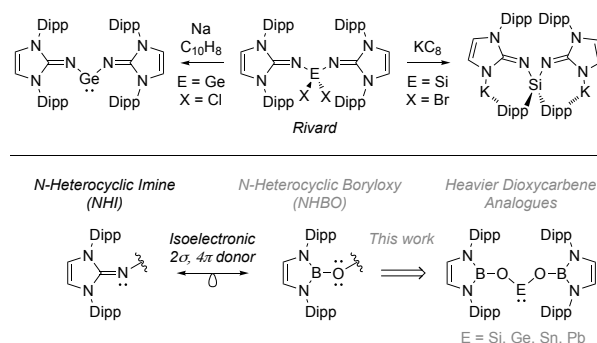
Scheme 1. (top) Rivard's synthesis of [(HCDippN)₂CN]₂Ge and attempted synthesis of [(HCDippN)₂CN]₂Si; (bottom) Isoelectronic relationship between [(HCDippN)₂CN]⁻ and [(HCDippN)₂BO]⁻ ligands, and syntheses of [(HCDippN)₂BO]₂E (E = Si - Pb). (Dipp = 2,6-diisopropylphenyl).

Isoelectronic with these target [(HCArN)₂BO]⁻ systems are *N*-heterocyclic iminato (NHI) ligands, [(HCArN)₂CN]⁻ - monoanionic N-donors possessing an exocyclic C=N double bond which are capable of acting as strong (2σ+4π) donors.[5] This attribute, in combination with a large steric profile has been exploited in the stabilization of low coordinate main group systems,[6] including an acyclic silanone.[6e] A small number of heteroleptic NHI-stabilized heavier carbene analogues have also been reported by Inoue and co-workers,[7] but the only homo-leptic NHI complex reported to date is [(HCDippN)₂CN]₂Ge synthesized by Rivard *et al.* (Scheme 1).[8] Attempts to synthe-size the corresponding silylene, [(HCDippN)₂CN]₂Si, generated instead a Si(IV) product via activation of the NHI ligand, potentially reflecting the fact that a wholly NHI donor framework renders the Si(II) centre too electron rich (high lying HOMO). We hypothesized that replacing the NHI ligands with a (slightly weaker σ donor) O-based analogue, such as [(HCDippN)₂BO]⁻, might offer access to a tractable homoleptic silylene. With this in mind, we introduce in this manuscript the *N*-heterocyclic boryloxy (NHBO) ligand class, and report on its use in the isolation of the first acyclic dioxysilylene.

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SI for this article is given via a link at the end of the document.

We first sought to systematically quantify the donor capabilities of the [(HCDippN)$_2$BO]$^-$ ligand in comparison with other oxy ligands and with NHIs (Figure 1). DFT calculations using the PBE1PBE hybrid exchange-correlation functional (see SI) on the 'free' anionic ligands are consistent with the isolobal nature of these systems: the HOMO and HOMO-1 in each case are the orthogonal in- and out-of-plane π donor orbitals, although their relative ordering varies according to the π acceptor capabilities of the O- or N-bound group. In general, the energies of the HOMO/HOMO-1 rise in the order [{(Me$_3$Si)$_2$HC}$_2$BO]$^-$, [(2,6-Dipp$_2$C$_6$H$_3$)O]$^-$, [(HCDippN)$_2$BO]$^-$, [(HCDippN)$_2$CN]$^-$, reflecting successively enhanced π donor abilities. The ligand σ donor capabilities are, as expected, somewhat diminished for all of the oxy systems compared to [(HCDippN)$_2$CN]$^-$ (cf. energies of −4.92 and −3.75 eV for the σ frontier orbitals of [(HCDippN)$_2$BO]$^-$ and [(HCDippN)$_2$CN]$^-$, respectively).

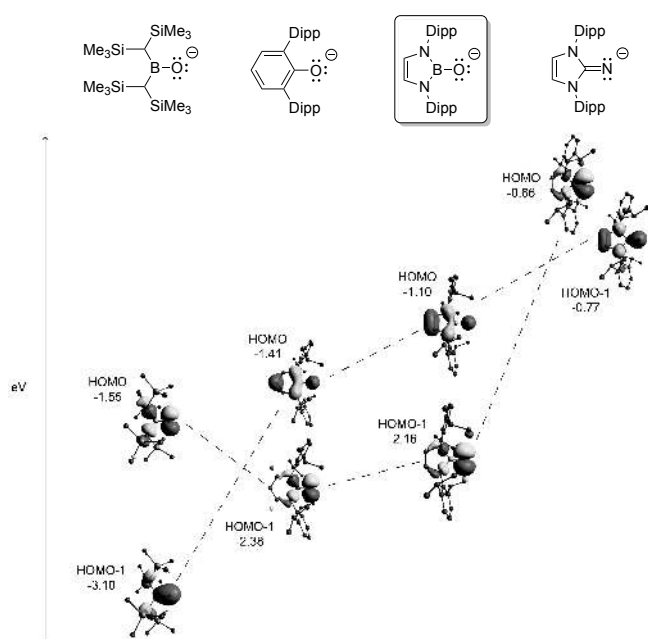**Figure 1.** Frontier orbitals and their relative energies for [{(Me$_3$Si)$_2$HC}$_2$BO]$^-$, [(2,6-Dipp$_2$C$_6$H$_3$)O]$^-$, [(HCDippN)$_2$BO]$^-$ and [(HCDippN)$_2$CN]$^-$ (isosurface 0.04).

With these predictions in mind, we sought a convenient synthesis for borinic acid ("protio ligand") **1**.[4d] Treatment of the corresponding bromoborane in a biphasic water/toluene mixture using pyridine as a base leads to facile introduction of the exo-cyclic OH group in 66% yield (Scheme 2). Subsequent deproton-ation was achieved by treating **1** with K[N(SiMe$_3$)$_2$] to afford K[(HCDippN)$_2$BO], **2**, which was recrystallized from *n*-hexane and shown by X-ray crystallography to be dimeric in the solid-state (see SI).

With **1** and **2** in hand, we set out to prepare a series of heavier group 14 dioxycarbene analogues. Unlike their cyclic counterparts, isolable acyclic silylenes are a relatively recent development – the first being reported in 2012.[9] To date only a handful of such systems are known and among this group, dioxysilylenes are conspicuously absent. Treatment of **2** with
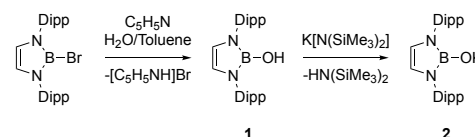
Scheme 2. Syntheses of (HCDippN)$_2$BOH (**1**), K[(HCDippN)$_2$BO] (**2**) and dioxysilylene **3**.

half an equivalent of SiI$_4$ allows access to the intermediate [(HCDippN)$_2$BO]$_2$SiI$_2$ which could subsequently be reduced at 80 °C with Jones' reagent, [(Nacnac)Mg]$_2$ (Nacnac = HC(MeCMesN)$_2$; Mes = 2,4,6-Me$_3$C$_6$H$_2$), to afford the target system [(HCDippN)$_2$BO]$_2$Si, **3** in 87% isolated yield (Scheme 3). **3** is thermally stable at temperatures up to 80°C over a period of several days. The ^{29}Si{^{1}H} NMR spectrum of **3** features a signal at δ_{Si} = 35.5 ppm, i.e. significantly high-field shifted compared to acyclic diamino- (204.6 ppm)[9e] and dithiolatosilylenes (285.5 ppm),[9b] but similar to Inoue's (iminato)siloxysilylene (58.9 ppm).[6e] X-ray crystallography confirms the two-coordinate nature of the Si(II) centre in **3** (Figure 2), which represents the first example of an acyclic two-coordinate dioxysilylene. The two Si−O bonds subtend an angle at Si1 (100.02(8)°), which is narrower than those found for acyclic silylenes bearing less electronegative substituents (e.g. 109.7(1)° and 116.9(1)° for [Dipp(Me$_3$Si)N](X)Si, where X = (HCDippN)$_2$B or (Me$_3$Si)$_3$Si, respectively),[9a,c] consistent with the tenets of Bent's rule. Comparison with [(HCDippN)$_2$CN](^{t}Bu$_3$SiO)Si, reveals a very similar angle at Si (103.56(8)°),[6e] but significantly shorter Si−O distances in the case of **3** (1.6074(14) and 1.6052(14) Å vs. 1.643(1) Å).[6e] This presumably reflects the fact that in **3** there are two O-donor ligands, while in [(HCDippN)$_2$CN](^{t}Bu$_3$SiO)Si the dominant π donor contribution comes from the more strongly electron-releasing NHI substituent.
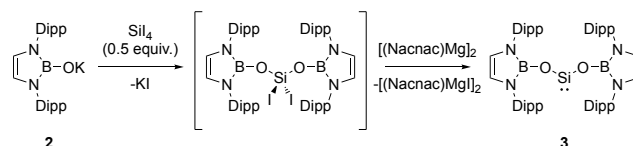
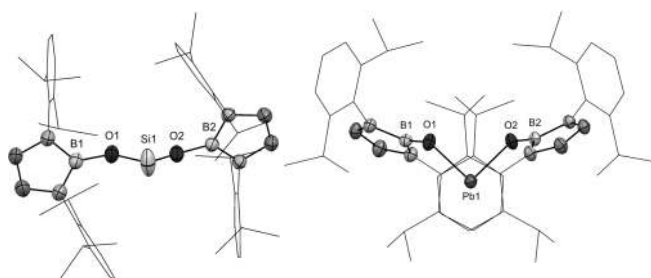**Scheme 3.** Synthesis of dioxysilylene **3**.

Figure 2. Solid-state structures of **3** (left) and **6** (right) as determined by X-ray crystallography. For clarity, hydrogen atoms are omitted and Dipp groups shown in wireframe format. Thermal ellipsoids are set at 40% probability. Selected bond lengths (Å): **3**: Si1−O1 1.6074(14), Si1−O2 1.6052(14), O1−B1 1.373(2), O2−B2 1.375(2). **6**: Pb1−O1 2.1319(16), Pb1−O2 2.1304(15), O1−B1 1.341(3), O2−B2 1.344(3) (for others see Table 1).

Following the synthesis of dioxysilylene **3**, we focused on its heavier congeners, which are conveniently accessed (for E = Ge, Sn, Pb) via a protonolysis route employing borinic acid **1** and 0.5 equivalents of $E[N(SiMe_3)_2]_2$ (E = Ge, Sn, Pb). These reactions afford the target metallylenes $[(HCDippN)_2BO]_2E$ in good yield (**4**: E = Ge (86%), **5**: E = Sn (88%), **6**: E = Pb (78%); Scheme 4). **5** is characterized by a $^{119}Sn\{^1H\}$ signal at δ_{Sn} = −109.0 ppm, which is downfield shifted from those of $[\{(Me_3Si)_2HC\}_2BO]_2Sn$ (−186 ppm)[3e] and $[(2,6-Dipp_2C_6H_3)O]_2Sn$ (−289.7 ppm).[1d] A similar trend is observed for **6**: the $^{207}Pb\{^1H\}$ NMR signal (δ_{Pb} = 1885 ppm) is shifted downfield compared to those of $[\{(Me_3Si)_2HC\}_2BO]_2Pb$ (1805 ppm)[3e] and $[(2,6-Dipp_2C_6H_3)O]_2Pb$ (1070 ppm).[1e]
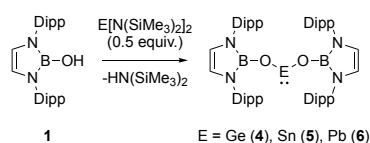
Scheme 4. Syntheses of $[(HCDippN)_2BO]_2E$ (E = Ge (**4**), Sn (**5**), Pb (**6**)).

All three compounds were characterized by X-ray crystallography (Figure 2, Figure 3 and SI) and shown to be isostructural with silylene **3** in the solid-state. Taking germylene **4** as an example, the O−Ge−O angle (93.56(7)°) is marginally wider than that of $[(2,6-Dipp_2C_6H_3)O]_2Ge$ (92.54(6)°),[1d] but narrower than that found in $[(HCDippN)_2CN]_2Ge$ (99.48(10)°).[8] In addition, the Ge−O bond distances (mean: 1.778(2) Å) are significantly shorter than those found in $[(2,6-Dipp_2C_6H_3)O]_2Ge$ (mean: 1.827(2) Å),[1d] consistent with the stronger π donor capabilities predicted for the boryloxy system. Similar trends are in evidence for **5** and **6**, with Sn−O and Pb−O distances (means: 2.015(2) and 2.131(2) Å) found to be shorter than in their aryloxy counterparts (means: 2.047(2) and 2.216(8) Å, respectively).[1d-e]

With a uniquely complete series of homoleptic group 14 heavier dioxycarbene analogues $[(HCDippN)_2BO]_2E$ in hand (E = Si, Ge, Sn, Pb), a number of periodic trends can be discerned (Table 1). Most obviously, on descending group 14, the O−E−O angle becomes more acute (approaching 90°) in line with the progressively less effective *s-p* mixing commonly observed for heavier main group elements.[2] In addition, the B−O distances shorten, consistent with increasing π donation from oxygen to boron as the competing O-to-E π interaction becomes less efficient; this hypothesis is consistent with the results of Wiberg bond index calculations (see SI). Consistently, the B−O distances in **3** (mean: 1.374(2) Å) are essentially identical to that found in **1** (1.373(3) Å),[4d] while those in **6** (mean: 1.343(3) Å) approach B−O separations in systems for which multiple bond character is claimed.[10] Most interestingly, the B−O−E−O torsion angles decrease as E becomes heavier, consistent with swiveling of the $[(HCDippN)_2BO]^-$ ligands so as to place one of the pendant Dipp groups of each diazaborolyl fragment above/below the central O−E−O plane (Figure 3). This enables enhanced arene π interactions between the Dipp groups and the formally vacant *p*π orbital of the central E(II) atom, and is also reflected in sequential shortening of the distances between E

and the respective *ipso*-carbon. The effect is most prominent in the case of plumbylene **6**, which features a mean Pb···C_{ipso} contact of 3.095(2) Å. Viewed from another perspective, the $[(HCDippN)_2BO]^-$ ligand might be regarded as showing aspects of ambidentate behaviour – based on hard (oxygen) and soft (Dipp/arene) donor sites.[11] On descending group 14, the central E(II) atom becomes increasingly polarizable (soft), leading to an increased propensity to interact with the softer arene donor site.

Table 1. Selected bond distances (Å) and angles (°) for $[(HCDippN)_2BO]_2E$ (E = Si, Ge, Sn, Pb).

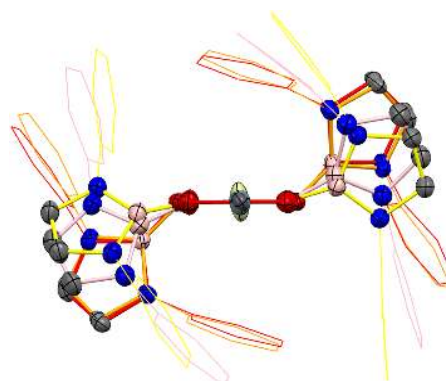|	O−E−O	E−O[a]	B−O[a]	B−O−E−O[a]	E−C_{ipso}[a]
3	100.02(8)	1.606(1)	1.374(2)	159.48(1)	3.576(2)
4	93.56(7)	1.778(2)	1.362(3)	144.45(1)	3.421(2)
5	93.25(8)	2.015(2)	1.353(3)	123.40(1)	3.123(2)
6	92.66(6)	2.131(2)	1.343(3)	120.37(1)	3.095(2)

[a] Mean values.

Figure 3. Solid-state structures of **3** (yellow), **4** (pink), **5** (orange) and **6** (red) overlaid. For clarity, hydrogen atoms and *i*Pr groups are omitted and Dipp groups shown in wireframe format. Thermal ellipsoids are set at 40% probability.

Finally, in order to understand the role of the $[(HCDippN)_2BO]^-$ ligand within complexes **3**-**6**, and in particular its ability to support an unprecedented class of silylene, we subjected these systems to DFT analysis using the PBE1PBE hybrid exchange-correlation functional (see SI). These calculations reveal that the LUMO in each case is comprised predominantly of E p_z character, with increasingly minor O p_z contributions on descending the group (consistent with the diminished role of E−O π bonding). The HOMO is typically ligand-based, with orbitals displaying E-centred lone pair character being the HOMO-2 (at ca. −6.69 eV for E = Si, Ge and Sn), presumably due to the influence of the two highly electronegative α-O atoms. Intriguingly, in the case of **6**, the orbital possessing predominant Pb-centred lone pair character is the HOMO-10 (−7.46 eV), presumably stabilized due to relativistic effects. In line with expectations for systems featuring the $[(HCDippN)_2BO]^-$ ligand, the energetic separation between the E-centred lone pair and vacant *p*π orbital is very large for all E, a factor which presumably contributes to the stability of

acyclic silylene **3**. Thus for [(HCDippN)$_2$BO]$_2$Si, the calculated energy gap (5.45 eV) is considerably larger than those for previously reported acyclic silylenes (e.g. 4.33 and 4.23 eV for an (iminato)siloxy- and a dithiolatosilylene, respectively).[6e,9b]

In conclusion, we report on the development of a new class of strongly donating *N*-heterocyclic boryloxy (NHBO) ligand, isoelectronic with the well-known NHI family. Employment of this ligand enables the successful stabilization of the first acyclic two-coordinate dioxysilylene together with its heavier (Ge, Sn, Pb) congeners. While literature examples of low coordinate main group species are predominantly supported by N-based ligands, those based on O-donors are conspicuously rarer. We foresee that this class of NHBO ligand, with its strong donor capacity and large steric profile will provide an entry point to access other thermodynamically robust oxy-stabilized main group species.

Experimental Section

General experimental procedures, synthetic and characterizing data for all new compounds, crystallographic and computational details are included in the Supporting Information. CIF files for the five X-ray crystal structures have been deposited with CCDC (ref: 1873893-1873897).

Acknowledgements

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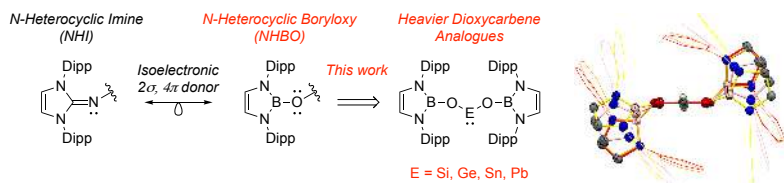
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An *N*-Heterocyclic Boryloxy Ligand Isoelectronic with *N*-Heterocyclic Imines: Access to an Acyclic Dioxysilylene and its Heavier Congeners

Exploiting the isoelectronic relationship with *N*-heterocyclic imine (NHI), we introduce a new class of *N*-heterocyclic boryloxy (NHBO) ligand that is a strong O-donor. Employing the NHBO ligand, we present the first acyclic two-coordinate dioxysilylene and its heavier (Ge, Sn, Pb) congeners, which represents the first complete series of group 14 heavier dioxycarbene analogues.