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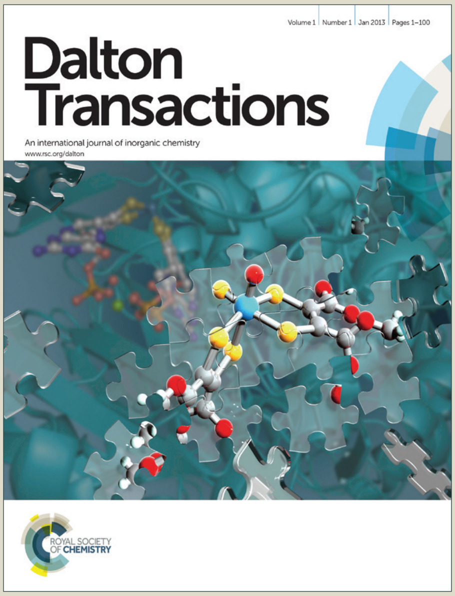

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Reactivity of a dihydroboron species: Synthesis of a hydroborenium complex and an expedient entry to stable thioxo- and selenoxo-boranes

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The reaction of a recently synthesized dihydroboron species complexed with bis(phosphinimino)amide, LBH_2 (**1**), (L = $[N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2]^-$) with 3 equivalents of $BH_2Cl{\cdot}SMe_2$ or one equivalent of BCl_3 affords the first stable monohydridoborenium ion, $[LBH]^+[HBCl_3]^-$ (**2**) that is stable without a weakly coordinating bulky anion. Compound **2** can also be prepared directly by refluxing LH with 3 equivalents of $BH_2Cl{\cdot}SMe_2$. Interestingly, reaction of LBH_2 (**1**) with elemental sulfur and selenium involves oxidative addition of S and Se into B-H bonds and subsequent release of H_2S (or H_2Se) from the intermediate $LB(SH)_2$ (or $LB(SeH)_2$) species forming stable compounds with terminal boron-chalcogen double bonds LB=S (**3**) and LB=Se (**4**). The electronic structures of compounds **2**, **3** and **4** were elucidated by high resolution mass spectrometry, multi-nuclear NMR and single crystal X-ray diffraction studies. Ab initio calculations on **3** are in excellent agreement with its experimental structure and clearly support the existence of boron-sulfur double bond.

Introduction

In recent times, a few Lewis acid stabilized oxoborane species containing terminal B=O have been realized.[1-4] Braunschweig and co-workers reported the first Lewis acid free boron-oxygen triply bonded compound supported by a late transition metal fragment.[5a,b] Thioxoborane, RB=S; selenoxoborane, RB=Se; thiols (R_2BSH & $RB(SH)_2$ and selenols (R_2BSeH & $RB(SeH)_2$) are still considered to be elusive species and stable forms of these compounds are much sought after.[6-8] Although the involvement of thioxoborane was first recognized almost 20 years ago in trapping experiments of the transient Tbt-B=S with 1,3-butadienes for [4+2]cycloaddition reactions[8] (Tbt = 2,4,6-tris{bis(trimethylsilyl)methyl}phenyl), high reactivity and lack of facile synthetic approaches have limited the isolation of species stable at room temperature. Till date only one example each of neutral thioxo- and selenoxo-borane compound, $[HC(CMe)_2(N\text{-}2,6\text{-}Me_2C_6H_3)_2]B{=}E$ (E = S, Se) is available in the literature.[9] Whereas, a boron cation with boron-sulfur double bond supported by a bulky *bis*(imidazolin-2-iminato) ligand is reported recently.[10] The corresponding Se analogue has not been reported as yet. Therefore, we believe that synthesis and characterization of stable molecules of boron containing thiol & selenol functionality and boron doubly bonded with S and Se is an important step towards rationalization of electronic structure, bonding, and chemical reactivity of this class of compounds.

The lack of a suitable starting material and a rational synthetic route are major synthetic challenges in this area. The alkyl or aryl borinic (R_2BOH) and boronic ($RB(OH)_2$) acids[11] are easily prepared and have been used extensively in organic synthesis as building blocks and as intermediates in Suzuki coupling.[12] Additionally, the dihydroxyborenium cation $[NHC\text{-}B(OH)_2]^+TfO^-$ is also known.[13] In contrast, the thio- and seleno-boric acids derivatives, R_2BEH and $RB(EH)_2$ are not much explored (E = S, Se).[14-18] These heavy analogues of borinic and boronic acids are generally detected in the reactions of halogenoboranes with H_2E.[14] The thio derivatives after loss of H_2S generate diborylsulfanes $(R_2B)_2S$ and can also rearrange into borthiins $(RBS)_3$ and tri-organylboranes.[14] The Se analogues of these compounds are even rarer; the compounds $BX_{3-n}(SeH)_n$ (X = Cl, Br, I) have been studied by vibrational spectroscopy.[18] The oxidative addition of S and Se into the Al-H bonds in alanes has been established and could be an alternative route to prepare the B-EH or $B(EH)_2$ derivatives (E = S, Se).[19] If isolated these thio- and seleno-boric acids derivatives can be important precursors for the synthesis of neutral and cationic thioxo- and selenoxo-borane compounds.

Recently, we reported on the synthesis and characterization of a dihydroboron species, LBH_2 (**1**) complexed with a bulky monoanionic bis(phosphinimino)amide ligand (L = $[N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2]^-$).[20] Selection of bis(phosphinimino) amide as ligand was deliberate to mitigate against the known tendency of easy H migration from/or to the

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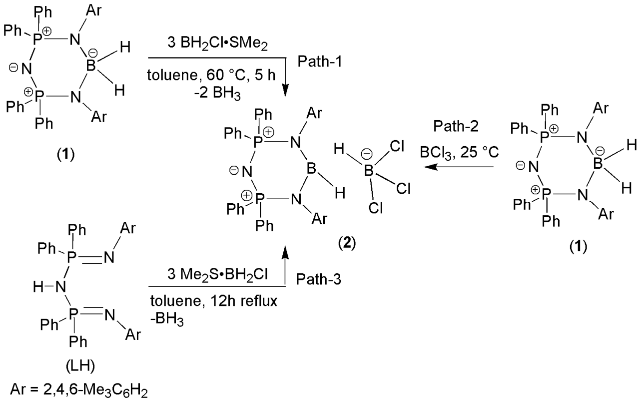
† Electronic supplementary information (ESI) available: Multinuclear NMR spectrum of compound **2-4**. CCDC reference number 1403909, 1054676 and 1054677 for compounds **2-4**, respectively are available. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

boron atom in boranes.[9] Treatment of compound **1** with 3 equivalents of $BH_2Cl{\cdot}SMe_2$ affords the hydroborenium species $[LBH]^+[HBCl_3]^-$ (**2**). We attempted oxidative insertion of elemental S (and Se) into the B-H bonds of compound **1** to explore the possibility of isolating a dithiol (and diselenol) and the addition of sulfur into the B-H bond of compound **2** to prepare a cationic mercaptoborane. Our efforts rewarded us with the discovery of a facile synthesis of doubly bonded terminal LB=S (**3**) and LB=Se (**4**) compounds under H_2S or H_2Se evolution from the corresponding dithiol or diselenol intermediate. However, reaction of compound **2** with sulfur leads to HCl evolution and formation of $[LH_2]^+Cl^-$ as the only isolable product.

Results and discussion

Reaction of LBH_2 (**1**) with three equivalents $BH_2Cl{\cdot}SMe_2$ in toluene at 60 °C (Path 1, Scheme 1) results in the formation of the hydroborenium species $[LBH]^+[HBCl_3]^-$ (**2**). To the best of our knowledge, compound **2** is the first example of a stable monohydridoborenium ion, containing a simple anion $BHCl_3^-$, that does not require a bulky weakly coordinating anion for stability.[21-23] Compound **2** has also been conveniently prepared by other alternative routes as shown in Scheme 1; *path 2* involving the reaction of **1** with one equivalent of BCl_3 and *path 3* by reacting LH with three equivalents of $BH_2Cl{\cdot}SMe_2$ at 110 °C. While the course of reaction is straightforward for *path 2* the reaction through *path 1* proceeds *via* hydride abstraction by the Lewis acid, BCl_3 formed *in-situ*, and BH_3 as the other possible product whereas *path 3* involves hydrogen evolution to first give LBHCl[25] which subsequently reacts with the second equivalent of $BH_2Cl{\cdot}SMe_2$ to generate $BH_2Cl_2^-$ that undergoes metathesis with the third equivalent of $BH_2Cl{\cdot}SMe_2$ to generate BH_3 and $BHCl_3^-$ counter anion. The only monohydridoborenium cation reported in the literature is dipyrromethene complexed with a substituted boron atom, $[(BODIPY)BH]^+$ that is stabilized by a bulky weakly coordinating anion, $[B(C_6F_5)_4]^-$.[24] Other notable hydrido boron cations include the hexaphenylcarbodiphosphorane stabilized dihydrido borenium cation, $[(Ph_3P)_2CBH_2]^+[HB(C_6F_5)_3]^-$ reported by Alcarazo and coworkers[26] and the work of Chen *et al.* on three coordinate BH_4^-, I^-, and OTf^- salts of dicationic hydrido boron complexes stabilized by carbodicarbene.[27]



Scheme 1 Synthesis of a hydroborenium cation, $[LBH]^+[HBCl_3]^-$ (**2**).

Compound **2** was characterized by spectroscopic, spectrometric, and single crystal X-ray techniques. The HRMS investigations under +ve ion mode of **2** revealed the signal at *m/z* = 662.3032 (calculated *m/z* = 662.3043) as the base peak corresponding to the cationic moiety $[M\text{-}BHCl_3]^+$. The IR spectrum of **2** showed the B–H stretch at 2545 and 2470 cm^{-1}.[20] In the ^1H NMR spectrum of complex **2** the B*H* resonance appeared as a broad signal around 4.27 ppm and other signals were consistent with the ligand backbone. A downfield shift in the $^{31}P\{^1H\}$ NMR spectrum of **2** (22.7 ppm) was observed when compared to LBH_2 (19.2 ppm).[20] The ^{11}B NMR spectrum of **2** showed a sharp doublet at 3.30 ppm with $^1J_{B\text{-}H}$ of 164.3 Hz, this signal can be attributed to the anionic moiety of **2**.[28] The signal for B atom of the cationic moiety is not detected perhaps due to the low local symmetry around this boron atom.

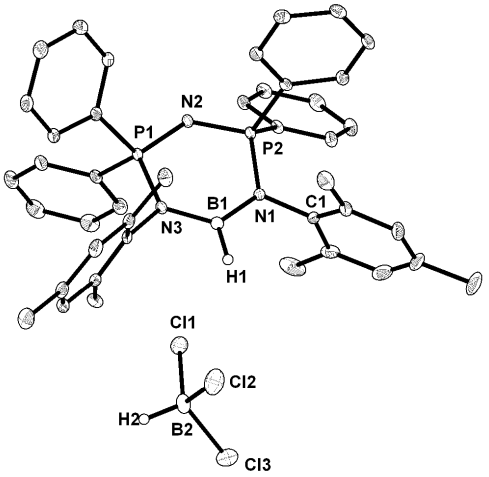
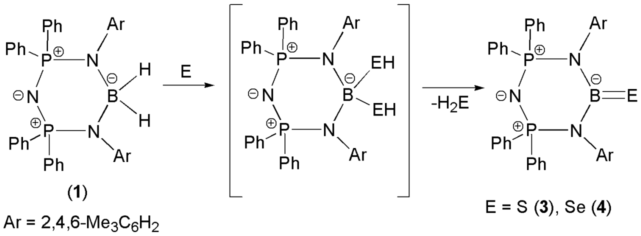


Fig. 1 Molecular structure of $[LBH]^+BHCl_3^-$ (**2**). All hydrogen atoms except on boron atoms have been deleted for clarity. Thermal ellipsoids have been drawn at 30% probability. Selected bond lengths (Å) and bond angles (°): B(1)–H(1) 1.110(2), B(1)–N(1) 1.432(5), B(1)–N(3) 1.437(1), N(1)–P(2) 1.680(2), N(2)–P(1) 1.580(5), N(2)–P(2) 1.579(1), N(3)–P(1) 1.679(4), B(2)–H(2) 1.070(3), B(2)–Cl(1) 1.866(2), B(2)–Cl(2) 1.839(3), B(2)–Cl(3) 1.866(2), N(1)–B(1)–N(3) 125.8(1), N(1)–B(1)–H(1) 118.5(1), N(3)–B(1)–H(1) 115.6(1), N(2)–P(2)–N(1) 107.8(1), N(2)–P(1)–N(3) 108.3(1), H(2)–B(2)–Cl(1) 111.4(1), H(2)–B(2)–Cl(2) 107.5(1), H(2)–B(2)–Cl(3) 110.8(1), Cl(1)–B(2)–Cl(2) 109.1(1), Cl(1)–B(2)–Cl(3) 109.2(1), Cl(2)–B(2)–Cl(3) 108.7(1).

Single crystals of **2** suitable for X-ray structural analysis were grown from toluene. Compound **2** crystallizes in the monoclinic crystal system with $P2_1/n$ space group (Fig. 1). In the solid state ion pairs of a molecule of **2** are well separated, probably due to bulky nature of the cationic moiety, and the molecules of **2** are also discrete showing no intermolecular interactions. The coordination environment around cationic boron is distorted trigonal planar whereas anionic part exhibits a distorted tetrahedral geometry. The central N_3P_2B ring in **2** slightly deviates from planarity. The B-H bond length (1.110(2) Å) in the cationic part of 2 is longer than the B-H distance in its counter anion (1.070(3) Å) and that reported in BODIPY derived borenium ion (0.950 Å).[24] The B-N distances in **2** (1.432(5) and 1.437(1) Å) slightly shorter than that in its precursor **1** (1.588(5) and 1.615(5) Å). The N(1)-B(1)-N(3) bond angle in **2** (125.75(1)°) is wider than the N-B-N bond angle in its precursor **1** (110.60(2)°).[20]

To investigate the reaction chemistry of the newly synthesized hydroborenium species, $[LBH]^+BHCl_3^-$ (**2**) oxidative addition of sulfur into the B-H bonds of it was attempted with an anticipation to isolate the cationic mercaptoborane compound, $[LBSH]^+BHCl_3^-$. The reaction of sulfur with compound **2** did not progress at room temperature however, under reflux conditions in toluene the insertion of sulfur presumably occurs converting the hydride into a thiol function which due to the presence of $HBCl_3^-$ anion releases HCl and formation of $[LH_2]^+Cl^-$ as the only isolable soluble product. Use of Et_3N or lutidine as bases in the reaction lead to the isolation of the mixture of ammonium salts and $[LH_2]^+Cl^-$.

The reaction of LBH_2 (**1**) with two equivalents of elemental S or Se in toluene at room temperature and at 80 °C respectively, resulted in complete consumption of the chalcogen with concomitant evolution of H_2S and H_2Se leading to the formation of LB=S (**3**) and LB=Se (**4**) (L = $[N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2]^-$) (Scheme 2) in good yields.[29] Thus, this synthetic method represents an attainable and rational route for the preparation of novel compounds with boron chalcogen double bonds. The intermediate dithiol (or diselenol) species turned out to be kinetically labile leading to intramolecular H_2S or H_2Se evolution.[10] This is presumably due to the wider N-B-N bite angle offered by the chelating bis(phosphinimino)amide ligand thus, bringing the two B-SH bonds in a proximity close enough to eliminate H_2S or H_2Se (*vide infra*).



Scheme 2 Synthesis of thioxoborane, LB=S (**3**) and selenoxoborane, LB=Se (**4**) compounds.

Compounds **3** and **4** have been unambiguously characterized by means of spectroscopic, spectrometric, and crystallographic techniques. Both **3** and **4** are thermally quite stable and undergo decomposition with melting at 187 and 190 °C, respectively. The HRMS investigations of **3** revealed the $[M\text{-}H]^+$ at m/z = 693.2664 (calculated m/z = 693.2675), similarly a peak at m/z = 742.2219 (calculated m/z = 742.2201) in **4** was also due to $[M^+]$. The IR spectrum of **3** showed a sharp band (1096 cm^{-1}) which can be assigned to the B=S fragment.[9] The corresponding stretching mode for **4** appeared at 1076 cm^{-1}.[9] The ^1H NMR resonance signals for **3** and **4** were in accordance with the ligand backbone and composition. No other appreciable signals were detected in the crude products which could be attributed to any residual/adventitious SH/SeH moiety. The $^{31}P\{^1H\}$ spectrum of **3** and **4** showed a sharp single resonance at 23.5 and 21.63 ppm respectively, which is downfield shifted as compared to its precursor **1** (19.2 ppm).[20] The ^{11}B NMR spectrum of **3** (and **4**) revealed a broad resonance at 41 ppm (and 45.2 ppm), suggesting a low local symmetry around the boron atom for three coordinated boron species.[9,10] This also excludes the possibility of any dimer formation (B_2S_2 core), due to [2+2] addition of the B=S bonds in the solution state. To rule out any H_2 evolution from the possible intermediate LB(SH)H species, leading to **3**, we performed a stoichiometric reaction between LBH_2 and S. To our surprise, as monitored by *in-situ* $^{31}P\{^1H\}$ NMR measurements, almost half of the starting material was consumed to form only **3** and the remaining half of LBH_2 was present unreacted. This not only supports the intramolecular evolution of H_2S but also suggests that the insertion of S in the B-H bond of LB(SH)H to be more facile than that in LBH_2 itself with concomitant release of H_2S from **3**. In this respect, the behaviour of Se analogue **4** was found to be similar to that of **3**.

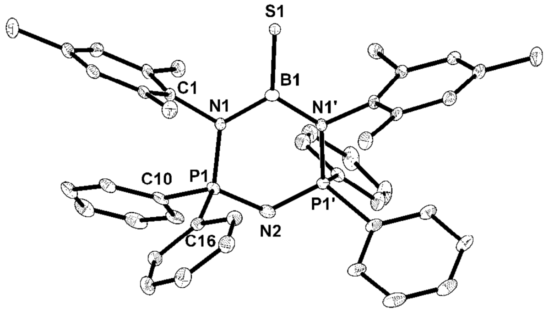


Fig. 2 Molecular structure of LB=S (**3**). All hydrogen atoms and THF molecule have been deleted for clarity. Thermal ellipsoids have been drawn at 30% probability. Selected bond lengths (Å) and bond angles (°): B(1)–S(1) 1.752(5), B(1)–N(1) 1.494(5), N(1)–P(1) 1.661(3), N(2)–P(1) 1.575(3), N(1)–B(1)–N(1‘) 117.10(2), N(1)–B(1)–S(1) 121.45 (1), N(2)–P(1)–N(1) 109.83(1), P(1)–N(2)–P(1‘) 128.77 (5).

Single crystals of **3** and **4** suitable for X-ray structural analysis were obtained, respectively, from their THF and toluene solutions. Compound **3** and **4** are found to crystallize in the orthorhombic space group *Pnc*2 and the tetragonal space group $I4_1/a$, respectively.

The X-ray crystal structures of **3** and **4** (shown in Fig. 2 and 3) are in agreement with spectroscopic and HRMS characterizations. Both the molecules possess boron atom in a three coordinated arrangement of a puckered N_3P_2B six-membered ring. Two terminal N atoms of the ligand and the doubly bonded terminal S (or Se) atom form the requisite bonds with the B atom. The two terminal N atoms and S (or Se) atom in compound **3** (and **4**) are bonded to the B atom in a trigonal planar arrangement (sum of angles at B is found to be 360°). The mesityl substituents on these terminal N atoms are oriented perpendicular to the N-B(S, Se)-N plane and provide necessary steric protection. The phenyl rings on the remote P atom of the ligand backbone are arranged above and below the P-N-P plane. The two phenyl rings attached to a P atom are approximately transverse to each other, with a dihedral angle of 65° between the two phenyl planes. On each P atom, one of the phenyl groups is in the same plane as the mesityl group attached to the diagonally opposite N atom. Interestingly, the central N atom on the ligand is in the same plane as N-B(S,Se)-N plane, with one of the P atom located above and the other P atom below this plane. The metric parameters observed in **3** and **4** are not unusual. The B(1)-S(1) bond length in compound **3** (1.752(8) Å) and B(1)-Se(1) distance in **4** (1.871(5) Å) are in agreement to that seen in the only known examples of this type, $[HC\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]BE$ (1.741(2) Å, E = S; 1.896(4) Å, E = Se).[9] The B-N distances among compound **3** and **4** are comparable and lie in the range (1.494(5)-1.498(6) Å) and agree with the reported values.[9] The delocalization of the negative charge on the ligand backbone is rather non-uniform as reflected in the two types of P-N bond lengths in both **3** and **4**. In compound **4** the terminal P-N distances 1.667(3) and 1.659(3) Å are slightly longer than the P(2)-N(2) and P(1)-N(2) bond length (1.578(3) and 1.577(3) Å) suggesting that the negative charge largely resides on the remote P-N-P moiety. The trigonal planar N_2BS and N_2BSe moieties in **3** and **4** respectively, exhibit the N-B-N bite angle of 117.10(2)° and 117.80(3)°. These angles are wider than the corresponding angle in **1** (110.60(2)°). This wider bite angle would certainly have its effect in bringing the two thiol (or selenol) groups in the intermediate $LB(EH)_2$ close enough to facilitate intramolecular evolution of H_2E (*vide supra*). The N-B-N angle of **3** and **4** is also wider than that in $[HC\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]BS$ (111.52°) and $[HC\{(CMe)(2,6\text{-}Me_2C_6H_3N)\}_2]BSe$ (112.6°),[9] respectively.

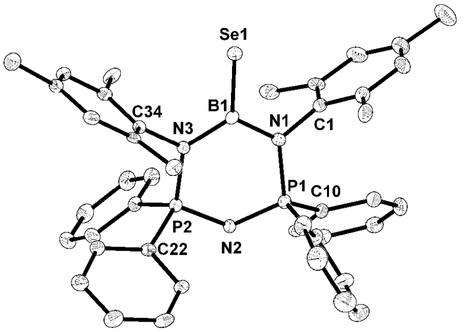
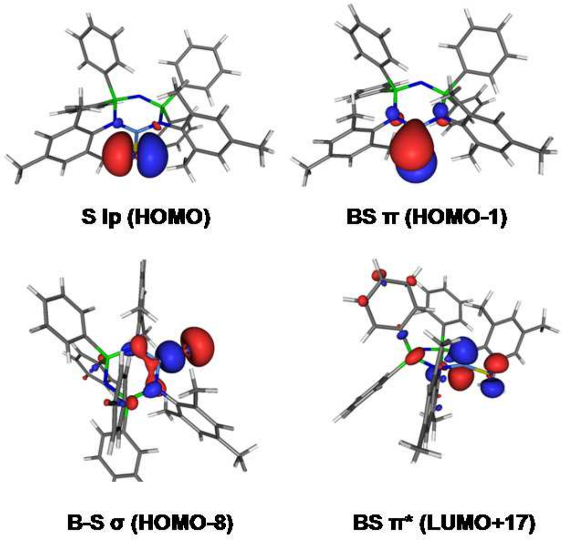


Fig. 3 Molecular structure of LB=Se (**4**). All hydrogen atoms have been deleted for clarity. Thermal ellipsoids have been drawn at 30% probability. Selected bond lengths (Å) and bond angles (°): B(1)–Se(1) 1.871(5), B(1)–N(1) 1.498(6), B(1)–N(3) 1.495(6), N(1)–P(1) 1.659(3), N(2)–P(1) 1.577(3), N(2)–P(2) 1.578(3), N(3)–P(2) 1.667(3), N(1)–B(1)–N(3) 117.8(3), N(1)–B(1)–Se(1) 121.4(3), N(3)–B(1)–Se(1) 120.8(3), N(2)–P(2)–N(3) 109.34(2), N(2)–P(1)–N(1) 109.67(2), P(2)–N(2)–P(1) 128.7(2).

In order to understand the geometric features of X-ray structures, we have performed a geometry optimization of compound **3** at B3LYP/cc-pVDZ level of theory. The optimized structure (see supporting information) correctly reproduces the experimental crystal structure (within 1-3 % for bond lengths and 0.5-1.5 % for bond-angles). The planarity of N_3BS unit, the extent of ring puckering, and the relative orientations of phenyl groups and mesityl groups are also well reproduced. All attempts to obtain alternate structures by geometry optimization starting with different orientations of phenyl and mesityl groups yielded the same optimized structure. This clearly shows that these geometrical features arise due to electronic factors.

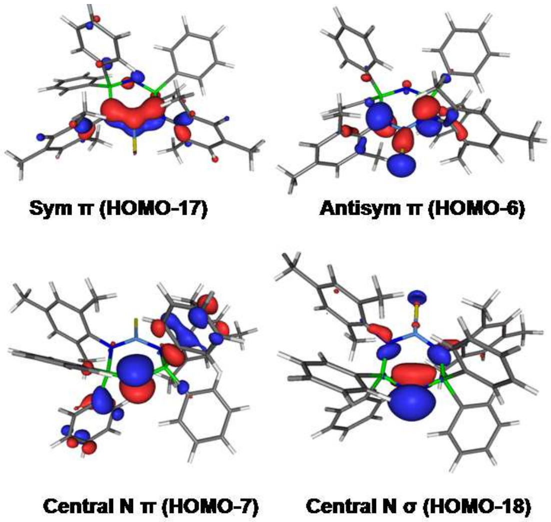
To gain further insight into the nature of bonding in these complexes, we make use of the delocalized Kohn-Sham (KS) orbitals along with localized orbitals produced through the natural bond orbital (NBO) analysis. The frontier KS orbitals involving the BS unit and the ligand atoms of the ring are plotted in Fig. 4. Clearly, the HOMO corresponds to sulfur lone pair, the HOMO-1 to the B-S π bond, and HOMO-8 to the B-S σ bond. The NBO calculation yields a σ orbital (1.976e) and a π orbital (1.966e) localized on B-S unit with strong polarization towards S. The NBO analysis shows a positive charge of +0.69e on B and a negative charge of -0.55e on S. Therefore, the B-S bond can be clearly considered as a polar double-bond. The NBOs corresponding to B-N bonds are in-plane nitrogen lone pairs (1.622e) with significant interaction with two boron-centered NBOs (0.438e, 0.474e) clearly confirming a B-N coordination bond.


S lp (HOMO) **BS π (HOMO-1)**

B-S σ (HOMO-8) **BS π* (LUMO+17)**

Fig. 4 Frontier Kohn-Sham orbitals on B=S unit of compound **3**.

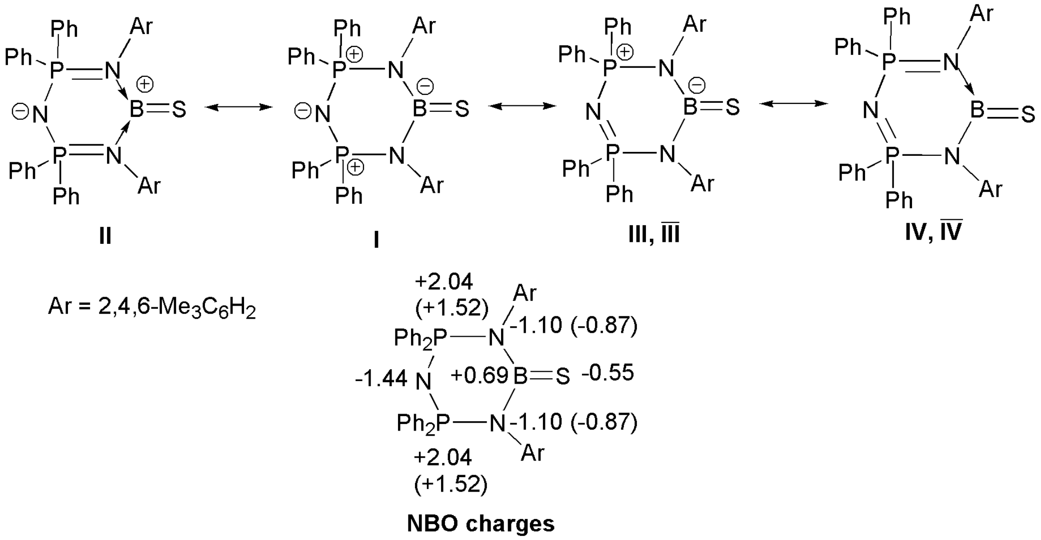
The three KS occupied π orbitals shown in Fig. 5 are mainly nitrogen centered with almost no contribution from phosphorus atoms. While two of these are centered on terminal nitrogen atoms with a partial delocalization over the B-S unit, the other one is mainly centered on the central nitrogen. The corresponding NBOs are found to be mainly nitrogen centered lone pairs. This indicates the absence of significant resonant delocalization of π electrons. A NICS value of [1.0 ppm] computed at the ring center also confirms the absence of aromaticity. The central and terminal nitrogens carry negative charge of -1.44e and -1.10e respectively, in contrast to positive charge of +2.04e carried by each phosphorus atom. An additional in-plane σ orbital mainly centered on the central nitrogen atom supports the view that this atom carries maximum negative charge.


Sym π (HOMO-17) **Antisym π (HOMO-6)**

Central N π (HOMO-7) **Central N σ (HOMO-18)**

Fig. 5 π orbitals of the N_3P_2B ring and σ orbitals of the central N of compound **3**.

Based on the X-ray data and results of geometry optimization and calculation of NBO charges several Lewis structures can be drawn for compound **3** (Scheme 3). Form **I** corresponds to a doubly iminophosphorane-stabilized species with a formal negative charge at the B atom. Positive charges at P atoms (phosphonium) and a negative charge at the central N atom maintain the electrical neutrality. Form **III** is similar to form **I** in a manner that it also represents an iminophosphorane-stabilized thioxoborane species with the negatively charged B atom and a formal positive charge at one of the P atom, whereas it differs from form **I** with respect to the central N−P−N portion of the ligand with other P atom forming a P=N with the central N atom. The short central P−N distances (1.575(3) Å) compared to terminal P−N distances (1.661(3) Å) as observed in X-ray are supportive of it. Form **II** being donor stabilized B=S fragment (thioxoborenium) possess a formal positive charge at the B atom and a negative chrge at the central N atom representing a zwitterionic structure of **3**. Form **IV** represents a neutral structure with terminal nitrogens forming a N→B donor and a N–B covalent bond and maintains the P−N distances in the ligand backbone between single (1.78 Å) and double (1.56 Å) PN bonds. Overall, a strong electron transfer from the two terminal N atoms to the $[B{=}S]^+$ fragment in compound **3** is indicated resulting in a stable thiooxoborane.



Scheme 3 Resonance structures for thioxoborane, LB=S (**3**), forms $\overline{\textbf{III}}$ and $\overline{\textbf{IV}}$ represent symmetrical resonance structure for the second half of **III** and **IV** respectively, and NBO charges. Numbers in the parentheses denote consolidated NBO charges whereas other numbers are bare NBO charges.

Conclusion

In conclusion, we have demonstrated rational synthetic strategies to obtain a hydroborenium cation stabilized by a bulky bis(phosphinimino)amide ligand without a need for a weakly coordinating bulky anion. A facile procedure for the preparation of terminal doubly bonded boron chalcogen compounds has also been discussed. We think that the resulting compounds LB=E (E = S or Se) are novel precursors to attempt interesting reaction chemistry. Currently, our efforts are focused on the preparation of tellurium analogue and preparation of a B(I) complex by reduction of **3** or **4**. Exploration of Lewis acid-base chemistry with these complexes and synthesis of BS anionic species are also underway.

Experimental section

Synthesis of $[\{N(Ph_2PN(2,4,6\text{-}Me_3C_6H_2))_2\}BH]^+BHCl_3^-$ (2): To a solution of LH (2.60 g, 4.0 mmol) in toluene (50 mL) at - 30 °C was added $BH_2Cl{\cdot}Me_2S$ (1.2 mL, 12 mmol, 10 M in Me_2S). The reaction mixture was brought to room temperature and was stirred for 2 hours followed by reflux for 12 hours. Evaporation of all volatile under vacuum afforded white solid that was washed with (2 x 20 mL) hexane and dried under vacuum. This material obtained was crystallized from toluene at room temperature. Yield: (2.81 g, 89.6 %). M.p. 175-177 ºC. IR (KBr): *ν* = 2545, 2470 (B-H stretch), 1587, 1438, 1328, 1296, 1191, 1116, 1023,726. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (s, *o*-C*H*$_3$, 12 H), 2.29 (s, *p*-C*H*$_3$, 6 H), 4.27 (broad, B*H*), 6.85 (s, 2,4,6-Me$_3$C$_6$*H*$_2$, 4 H), 7.65-7.54 (m, Ph, 16 H), 7.82-7.78 (m, Ph, 4 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6 (s, *o*-CH_3), 20.9 (s, *p*-CH_3), 125.7 (dd, $J_{C\text{-}P}$ = 125.0 & 2.0 Hz, aromatic), 129.4 (m not resolved, due to $J_{C\text{-}P}$ & $J_{C\text{-}B}$, aromatic), 130.6 (s, aromatic), 132.5 (m not resolved, due to $J_{C\text{-}P}$ & $J_{C\text{-}B}$, aromatic), 134.2 (s, aromatic), 134.9 (s, aromatic), 136.4 (s, aromatic), 139.0 (s, aromatic) ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 22.7 ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 3.3 (d, $^1J_{B\text{-}H}$ = 164.3 Hz) ppm. Mass spectrum (+ve ion, EI), *m/z* = calculated (found): 662.3032 (662.3043) $[M\text{-}BHCl_3]^+$.

Alternative syntheses for (2): (a) To a solution of LBH_2 (2.65 g, 4.0 mmol) in toluene (40 mL) at - 30 °C was added $BH_2Cl{\cdot}Me_2S$ (1.2 mL, 10 M in Me_2S, 12 mmol). The reaction mixture was brought to room temperature and was further heated at 60 ºC for 5 hours. Evaporation of all volatiles under vacuum afforded white sticky solid. This sticky solid was washed with (2 x 20 mL) hexane to give white solid. Yield: 2.62 g (84 %).

(b) To a solution of LBH_2 (2.65 g, 4.0 mmol) in toluene (40 mL) at - 30 °C was added BCl_3 (4 mL, 1 M in toluene, 4 mmol). The reaction mixture was brought to room temperature and was further stirred for 12 hours. Evaporation of all volatile under vacuum afforded white solid. Yield: 2.9 g (93 %).

Synthesis of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}B=S] (3): To a solution of LBH_2 (**1**) (1.98 g, 3.0 mmol) in toluene (50 mL) at 0 °C was added S_8 (192 mg, 6 mmol in 40 mL toluene). The initial clear solution became turbid and eventually yielded precipitate over a period of 24 hours of stirring at room temperature. This precipitate was isolated by filtration and washed with cold toluene on the filter stick to afford a white solid. This was crystallized from THF at -10 ºC. Yield: (1.35 g, 65 %). M.p. 187-190 ºC. IR (KBr): v = 526, 551, 568, 688, 724, 748, 828, 850, 945, 1001, 1050, 1096 (s, B=S), 1112, 1151, 1202, 1216, 1261, 1436, 1479, 2875, 2920 and 3046 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, *o*-CH_3, 12 H), 2.23 (s, *p*-CH_3, 6 H), 6.68 (s, 2,4,6-$Me_3C_6H_2$, 4 H), 7.31-7.36 (m, Ph, 8 H), 7.52-7.58 (m, Ph, 12 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4 (s, *o*-CH_3), 21.1 (s, *p*-CH_3), 127.9 (d, $J_{C\text{-}P}$ = 13.7 Hz, aromatic), 129.8 (dd, $J_{C\text{-}P}$ = 123.5 & 3.0 Hz, aromatic), 129.9 (s, aromatic), 132.5 (s, aromatic), 132.8 (d, $J_{C\text{-}P}$ = 11.2 Hz, aromatic), 135.9 (s, aromatic), 136.5 (s, aromatic), 138.2 (s, aromatic) ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 23.5 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 41.0 ppm (br). HRMS (+ve ion, EI), *m/z* = calculated (found): 693.2675 (693.2664) $[M–H]^+$.

Synthesis of [{N($Ph_2PNC_6H_2Me_3$-2,4,6)$_2$}B=Se] (4): Toluene (40 mL) was added to a flask containing **1** (1.326 g, 2.0 mmol) and elemental Se (0.32 g, 4.0 mmol) at room temperature. Heating at 80 ºC for 2 hours gave light greenish solution that was filtered while hot and pure **4** was collected as pale-green powder from this solution at room temperature. The mother liquor gave crystals of **4** at 4 ºC. Yield: (1.02 g, 69 %). M.p. 185-187 ºC. IR (KBr): v = 520, 539, 563, 695, 725, 747, 827, 851, 998, 1076 (s, B-Se), 1112, 1152, 1201, 1214, 1262, 1437, 1479, 2861, 2919 and 3050 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.85 (s, *o*-CH_3, 12 H), 2.23 (s, *p*-CH_3, 6 H), 6.69 (s, 2,4,6-$Me_3C_6H_2$, 4 H), 7.31-7.36 (m, Ph, 8 H), 7.53-7.58 (m, Ph, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (s, *o*-CH_3), 21.1 (s, *p*-CH_3), 128.0 (d, $J_{C\text{-}P}$ = 13.6 Hz, aromatic), 128.8 (d, $J_{C\text{-}P}$ = 2.8 Hz, aromatic), 130.0 (s, aromatic), 132.6 (s, aromatic), 132.9 (d, $J_{C\text{-}P}$ = 11.1 Hz, aromatic), 136.2 (s, aromatic), 136.9 (b, aromatic), 138.3 (s, aromatic) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 21.6 ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): δ = 45.2 (br) ppm. HRMS (+ve ion, EI), *m/z* = calculated (found): 742.2201 (742.2219) $[M^+]$.

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