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Title: Reactivity of a dihydroboron species: synthesis of a hydroborenium complex and an expedient entry into stable thioxo- and selenoxo-boranes

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Keywords: dihydroboron species
hydroborenium complex
thioxo- and selenoxo-boranes

Issue Date: 2015

Publisher: Royal Society of Chemistry

Citation: Dalton Transactions, 44(36)

Abstract: The reaction of a recently synthesized dihydroboron species complexed with bis(phosphinimino)amide, LBH₂ (1), (L = [N(Ph₂PN(2,4,6-Me₃C₆H₂))₂]-) with 3 equivalents of BH₂Cl·SMe₂ or one equivalent of BCl₃ affords the first stable monohydridoborenium ion, [LBH]⁺[HBCl₃]⁻ (2) that is stable without a weakly coordinating bulky anion. Compound 2 can also be prepared directly by refluxing LH with 3 equivalents of BH₂Cl·SMe₂. Interestingly, reaction of LBH₂ (1) with elemental sulfur and selenium involves oxidative addition of S and Se into B–H bonds and subsequent release of H₂S (or H₂Se) from the intermediate LB(SH)₂ (or LB(SeH)₂) species forming stable compounds with terminal boron–chalcogen double bonds LB[double bond, length as m-dash]S (3) and LB[double bond, length as m-dash]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 the boron–sulfur double bond.

URI: <https://pubs.rsc.org/en/content/articlelanding/2015/dt/c5dt02788h#divAbstract>
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