EurJIC
European Journal of Inorganic Chemistry

Communication
doi.org/10.1002/ejic.202000596

Diboranes | *Very Important Paper* |

A Facile Synthesis of Robinson's NHC-Stabilised Diborane(4)

Michael Trose,[a] David B. Cordes,[a] Alexandra M. Z. Slawin,[a] and Andreas Stasch*[a]

Abstract: Reactions of bis(pinacolato)diboron (B_2pin_2) with [(IDip)AlH_3] {IDip = $(HCNDip)_2C$:, Dip = 2,6-$iPr_2C_6H_3$} afforded both the new diborane [(IDip)BH_2B(pin)] and the known compound [(IDip)BH_2BH_2(IDip)] in a facile one-pot procedure; the latter reaction is improved by the addition of free IDip. [(IDip)AlH_3] transfers both IDip and hydride ligands to the diborane moiety in a halide-free approach. [(IDip)BH_2B(pin)] was structurally and spectroscopically characterised and additional spectroscopic data for [(IDip)BH_2BH_2(IDip)] is reported.

Diboranes[1] with a boron-boron single bond, such as the commercially available bis(pinacolato)diboron (B_2pin_2), are commonly employed reagents in synthetic chemistry for numerous borylation reactions,[1–4] and their further conversion of the resulting C–B fragments allows the transformation into a wide range of functional groups.[1,4] Diboranes with three-coordinate boron centres can be activated by the coordination of anionic ligands or neutral σ-donors, e.g. N-heterocyclic carbenes (NHCs), to sp^2-sp^3 diboranes.[1,4,5] The application of NHCs in boron chemistry[6] has furthermore led to the synthesis and isolation of a range of unusual low oxidation state molecules,[7] including diadducts of diboron species such as B_2H_4,[8] B_2H_2,[8,9] and B_2,[10] see Figure 1 for selected examples involving the sterically demanding NHC IDip [= $(HCNDip)_2C$:, Dip = 2,6-$iPr_2C_6H_3$]. The products **1**–**3** were obtained from reduction reactions involving very strong alkali metal-based reducing agents and the BH moieties in **1** and **2** resulted from uncontrolled hydrogen abstraction reactions likely of solvent molecules. Highly reactive congeners of **3** have subsequently been hydrogenated under mild conditions in high yields to congeners of **2**,[9c] but no facile route to **1** has yet been reported. Related phosphine adducts of B_2H_4 have been reported that were obtained from a higher triborane species.[11] Here we report on a simple alternative preparation of Robinson's NHC-stabilised diborane(4), **1**, starting from the commercially available boron(II) compound bis(pinacolato)diboron.

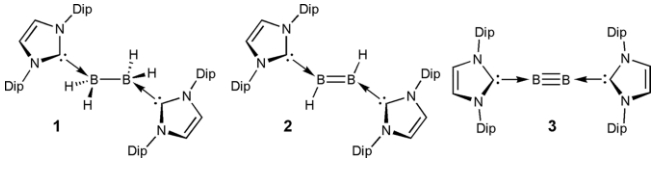
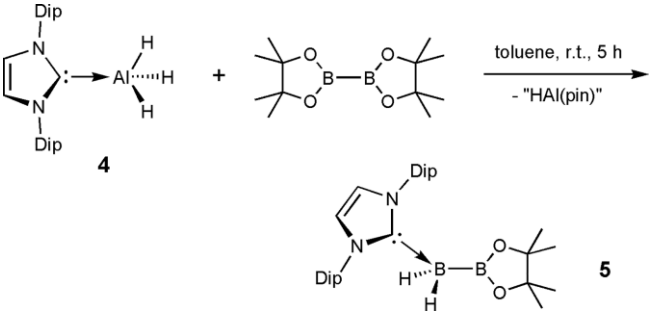


Figure 1. Examples of IDip-stabilised diboron species.

The reaction of stoichiometric amounts of [(IDip)AlH_3] **4**[12] with one equivalent of B_2pin_2 in deuterated benzene at room temperature was monitored by ^1H and ^{11}B NMR spectroscopy and showed the emergence of new resonances for one IDip-containing compound in the ^1H NMR spectrum alongside smaller resonances for some free IDip in an approximate 3:1 ratio. After approximately five hours, all [(IDip)AlH_3] (**4**) was consumed according to ^1H NMR spectroscopy, and the main new product formed in > 70 % yield shows one imidazolylidene CH resonance at δ = 6.37 ppm, and two doublets (δ = 1.04 and 1.44) and one septet (δ = 2.81) for the protons of the IDip isopropyl groups. Moreover, ^{11}B NMR spectroscopy revealed one broad resonance at 40.1 ppm and a poorly resolved triplet at –38.0 ppm suggesting an asymmetrically substituted diborane species with both three- and four-coordinate boron centres.[1,4,5] Performing a larger scale reaction in toluene at room temperature, followed by removal of all volatiles, extraction of the residue into *n*-hexane and crystallisation at 4 °C afforded [(IDip)BH_2B(pin)] (**5**) in 45 % isolated yield as a colourless crystalline material, see Scheme 1. During extraction with *n*-hexane, an insoluble gel-like residue formed as a by-product, presumably a polymeric material of approximate "HAlpin" composition.



Scheme 1. Synthesis of **5**.

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.202000596.

Compound **5**·0.5C_6H_6 was studied by single-crystal X-ray diffraction and crystallised with a full molecule in the asymmetric unit (see Figure 2) showing a B1–B2 bond length of 1.685(5) Å {cf. 1.686(4) Å in [(IMes)BH_2B(cat)]}, IMes = [(HCNMes)$_2$C:, Mes = 2,4,6-$Me_3C_6H_2$, cat = catecholato],[13] and a B1–C1 bond lengths of 1.592(5) Å {cf. 1.605(3) Å in [(IMes)BH_2B(cat)]}. [(IMes)BH_2B(cat)] and [(IDip)BH_2B(cat)] were previously prepared by the reaction of the respective NHC adduct of B_2cat_2 with BCl_3 to afford [(IMes)BCl_2B(cat)] or [(IDip)BCl_2B(cat)] followed by hydrogenation using two equivalents of tri-*n*-butyltinhydride and 10 mol-% sodium tetrakis(3,5-dichlorophenyl)borate.[13] Also, hydride abstraction of related [(IMe)BH(Mes)B(pin)] {IMe = (MeCNMe)$_2$C:} leads to a cationic diborane species that activates dihydrogen at low temperatures.[14]

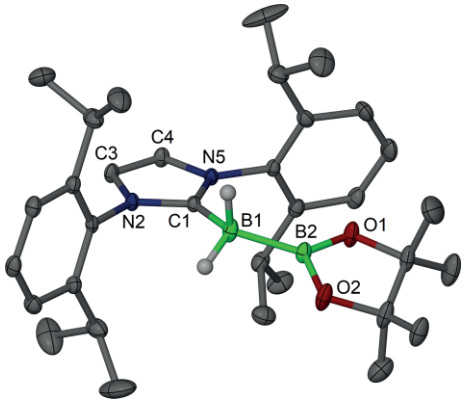
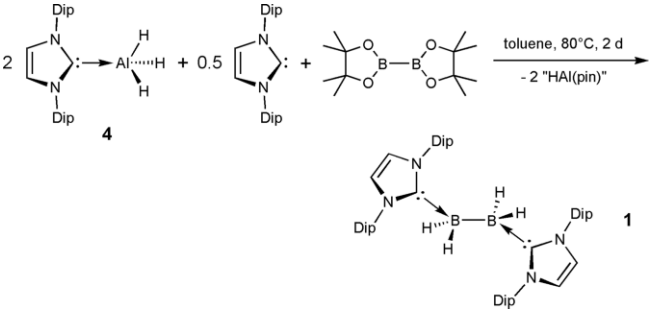


Figure 2. Molecular structures (25 % thermal ellipsoid) of [(IDip)BH_2B(pin)]·0.5C_6H_6, **5**·0.5C_6H_6. Only B–H hydrogen atoms are shown. Minor disordered isopropyl methyl groups and solvent molecule not shown for clarity. Selected bond lengths [Å] and angles (°): B1–B2 1.685(5), B1–C1 1.592(5), C1–N2 1.356(4), C1–N5 1.355(4), B2–O1 1.365(5), B2–O2 1.394(5); C1–B1–B2 124.6(3).

After successfully employing [(IDip)AlH_3] (**4**) to transfer both the IDip carbene ligand to boron and substitute hydride ligands for the pinacolato moiety with retention of the B–B bond, we studied other ratios of **4** with B_2pin_2 to evaluate if Robinson's NHC-stabilised diborane(4) compound [(IDip)BH_2BH_2(IDip)] (**1**) can be directly prepared in a one-pot procedure. A reaction of two equivalents of **4** with B_2pin_2 in deuterated benzene at room temperature afforded only traces of **1** after three days, as supported by the reported ^{1}H and ^{11}B NMR resonances.[8b,8d] Similar experiments carried out at 50 °C or 80 °C afforded mixtures mainly containing [(IDip)AlH_3] (**4**), [(IDip)BH_2B(pin)] (**5**) and [(IDip)BH_2BH_2(IDip)] (**1**) in varying ratios, for example with approximately 50 % of **1** after one day at 80 °C. It is notable that no resonances of free IDip were observed unlike in reaction mixtures for the synthesis of **5**, vide supra. We have previously found that mixtures of [(IDip)AlH_3] (**4**) and IDip show an equilibrium in deuterated aromatic solvents and hence only one set of resonances for the IDip fragment is found.[15] As the extremely broad resonance for the AlH_3 hydrogens cannot easily be integrated in a reliable manner, it is difficult to judge the true ratio of **4** to IDip in the reaction mixtures. Because [(IDip)AlH_3] (**4**) can be prepared from $LiAlH_4$ and IDip,[12] we added $LiAlH_4$ to study whether an additional hydride source can increase the yield of [(IDip)BH_2BH_2(IDip)] (**1**). However, no significant improvement in the ratio of the formation of **5** and **1** was observed from these experiments. Conversely, we tested the influence of additional free carbene IDip on the formation by reacting two equivalents of **4** with one equivalent of B_2pin_2 and half an equivalent of IDip in deuterated benzene. Heating these mixtures for three days at 50 °C or two days at 80 °C afforded reaction mixtures that mainly contained [(IDip)BH_2BH_2(IDip)] (**1**) in approximately 70 % in-situ yield alongside resonances of free IDip which may contain contributions from [(IDip)AlH_3] (**4**).[15] A reaction on a small preparative scale in this stoichiometric ratio in toluene at 80 °C for two days afforded, after extraction into *n*-hexane to remove the insoluble gel-like "HAlpin", **1** in 47 % isolated yield after crystallising at 4 °C, see Scheme 2.



Scheme 2. Synthesis of **1**.

The addition of free IDip may aid in the activation of the diborane, either B_2pin_2 and/or **5**, by coordination to a three-coordinate boron centre.[1,4,5] This would lengthen and weaken the B–O bonds and thus aid in substitution of the pinacolato groups in combination with using an oxophilic Al reagent that is also a good hydride source. Comparing bond lengths in structurally characterised imidazolylidene adducts of B_2pin_2 to those of uncoordinated B_2pin_2 shows the expected elongation of the B–O bond from ca. 1.38 Å in B_2pin_2 by ca. 0.1 Å (ca. 7 %) in its mono-NHC adducts, whereas the effect on the longer B–B bond is only ca. 0.03 Å (ca. 2 %).[4,5] Thus, we propose a mechanism where [(IDip)AlH_3] (**4**) coordinates to the pinacolato moiety on an IDip coordinated boron centre followed by hydride transfer to boron and full pinacolate substitution, see Figure 3 for a proposed intermediate. This would form [(IDip)AlH(pin)] or a very similar species that likely degradates to insoluble "HAlpin" and regenerates free IDip that is catalytically employed in the reaction. Inspecting reported RAl(pin) complexes shows that these appear to be only soluble when an excess of alkyl to pin groups are present, i.e. in structurally characterised

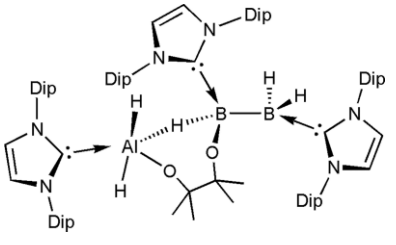


Figure 3. Proposed intermediate in the formation of **1**.

$[(Me_2Al)_2(pin)_2(AlMe)]$ which was isolated from other insoluble species, or when bulky *tert*-butyl groups are employed.[16] Free IDip was also observed in reaction mixtures forming **5** and therefore a similar mechanism is possible for its formation. Other exchange reactions of the pinacolate groups for B_2pin_2 are known, for example using Grignard reagents[17] or involving Lewis acidic BBr_3.[5b]

In our hands, $[(IDip)BH_2BH_2(IDip)]$ (**1**) was obtained as a pale-yellow crystalline material, cf. the closely related yellow dialane(4) complex $[(IDip)AlH_2AlH_2(IDip)]$,[18] and showed the same unit cell parameters from single-crystal X-ray crystallography as already reported.[8b,8d] The NMR spectroscopic data of **1** matched those reported previously,[8b,8d] with two sharp doublets and one sharp septet for the protons of the isopropyl groups in the ^1H NMR spectrum. In addition, we found a weak ^{13}C NMR IDip-carbene resonance at 187.9 ppm for **1** (cf. 179.7 ppm for **5**). For the broad BH_2 triplet in its ^{11}B NMR spectrum, we determined a B–H ^1J coupling constant of approximately 80 Hz. The BH resonances in **1** and **5** are difficult to detect by standard ^1H NMR spectroscopy, could not be found for **5**, and have not previously been reported for **1**. An $^1H\{^{11}B\}$ NMR spectrum recorded for $[(IMes)BH_2B(cat)]$ allowed an additional singlet at δ = 0.68 ppm to be detected.[6,13] The room temperature ^1H NMR spectrum of **1** shows no obvious BH resonances, although the presence of an extremely broad resonance at around δ = 0.5 ppm can be deduced. We have studied compound **1** in deuterated toluene by ^1H NMR spectroscopy between 295 K and 193 K. Over this range, the resonances for the isopropyl hydrogen environments appear as two doublets and one septet, are remarkably unchanged and do not significantly broaden, even though the very low temperature spectra show the ^3J coupling poorly resolved. This shows that the average structure of **1** in solution is highly symmetrical even at 193 K and suggests a flexible NHC→B_2H_4←NHC moiety. Over this temperature range, the broad BH resonance changes in appearance (see Figure S7), showing either multiple maxima or one broad resonance (243 K), but does not further resolve. IR spectra show a main BH stretch at 2344 cm^{-1} for **1** and stretches centred around a main band at 2322 cm^{-1} for **5**, which are within the range of those found for $(NHC)BH_3$ and related compounds.[6]

In summary, $[(IDip)BH_2BH_2(IDip)]$ (**1**) and $[(IDip)BH_2B(pin)]$ (**5**) can be conveniently prepared from $[(IDip)AlH_3]$ (**4**), commercially available B_2pin_2, plus some additional IDip in the case of **1**, in a halide-free approach. The NHC aluminium hydride **4** transfers both IDip and hydride ligands to the diborane unit and breaks the strong B–O bonds (ca. 590 kJ/mol) of the chelating dianionic pin ligand instead of the weaker B–B bond (ca. 435 kJ/mol).[19] Compound **5** was structurally and spectroscopically characterised and a variable temperature ^1H NMR study suggests that **1** shows a highly flexible average structure in solution even at –80 °C.

Deposition Number 2010683 (for **5**·0.5C_6H_6) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Supporting Information (see footnote on the first page of this article): Experimental details, NMR and IR spectra, X-ray crystallographic and refinement details.

Acknowledgments

We thank the University of St Andrews.

Keywords: Aluminum · Diboranes · Group 13 elements · Hydrides · Carbene ligands

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Received: June 22, 2020

Communication
doi.org/10.1002/ejic.202000596

Diboranes

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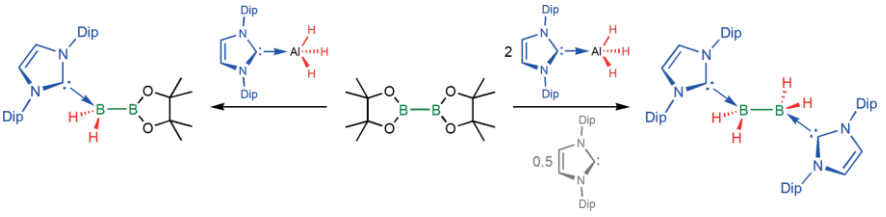
A Facile Synthesis of Robinson's NHC-Stabilised Diborane(4)



Bis(pinacolato)diboron reacts with the NHC aluminium hydride [(IDip)AlH_3] in a one-step protocol to [(IDip)BH_2B(pin)] and [(IDip)BH_2BH_2(IDip)]. [(IDip)AlH_3] transfers both hydride and NHC ligands to the diborane moiety in a halide-free approach and the ligand exchange process to the diborane(4) complex is enabled by the addition of free NHC ligand.

doi.org/10.1002/ejic.202000596