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Hydroboration of vinyl halides with mesitylborane : a direct access to (mesityl)(alkyl)haloboranes[§]Marc Devillard^{*a}, Marie Cordier,^a Thierry Roisnel,^a Chiara Dinoi,^b Iker Del Rosal,^b Gilles Alcaraz^{*a}Received 00th January 20xx,
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The direct access to (mesityl)(alkyl)haloboranes (Mes(Alk)BX) (X = Br, Cl) from mesitylborane dimer and vinyl halides is presented. The involved hydroboration reaction results in the transfer of the halogen atom from the carbon of the starting material to the boron in the final product. The reactivity of the obtained Mes(Alk)BX has been evaluated for the synthesis of the bipyridyl boronium cations and 2-arylpyridine derived boron N⁺C⁻-chelates. The formation mechanism of Mes(Alk)BX is appended by DFT-calculations which shows that their formation involves two concomitant pathways derived from the regioselectivity of the hydroboration reaction.

Molecular species incorporating main group heteroatoms play a key role in many areas of chemistry providing a value-added in terms of reactivity and properties.¹ Organoboranes, in particular, are proven modular intermediates that offer a range of synthetic possibilities due to their intrinsic reactivity.² With a formally empty p-orbital at boron, they exhibit a more or less marked electrophilic character that strongly depends on the boron atom connectivity pattern. The stepwise installation of substituents on a B_{sp2} centre while preserving a high Lewis acidity remains an actual challenge driven by the strong interest in boron-containing responsive materials and π systems,^{1a-c, 3} not to mention the recent development of frustrated Lewis pair chemistry where boranes play a prominent role.⁴ In this context but upstream of all this, (aryl)haloboranes have proven to be essential synthesis intermediates to build these molecular architectures.⁵ (Aryl)dihaloboranes (Ar-BX₂) are most widely obtained from trihalogenoborane (BX₃, X = F, Cl, Br, I) by Si/B or Sn/B exchange reactions involving the C_{sp2}-E (E = Si, Sn) bond of an arylsilane or -stannane.^{3b, 3g, 6} The reaction with more reactive

aryllithium or aryl-Grignard reagents is generally not easily controllable except in the case of extremely hindered reagents.^{3a, 3b, 3h, 7} Alternative pathways involving aryl-copper,⁸ -cadmium or mercury derivatives⁹ have also been reported but remain more scarce. Concerning (diaryl)haloboranes (Ar₂BX), their synthesis follows the same strategy from (aryl)dihaloboranes (Ar-BX₂) or trihalogenoboranes (BX₃) as the boron precursor. Surprisingly, while (aryl)(amino)haloboranes [Ar(R₂N)B-X] are well known and easily obtained from (aryl)dihaloboranes and amino derivatives¹⁰ or from (amino)dihaloboranes (R₂N-BX₂) in the presence of arylmetal and related reagents,¹¹ mixed (aryl)(alkyl)haloboranes [Ar(Alk)BX] are limited to only a few (aryl)benzylchloroborane¹² and (aryl)fluorenylchloroborane¹³ obtained from alkyldichloroboranes and aryl potassium or diaryl mercury reagents, respectively. Although C_{sp2}-E (E = Si, Sn) bonds are expected to react faster in B/Si or B/Sn exchange processes, the reaction involving C_{sp3}-E (E = Si, Sn) bonds was also found effective, although chemoselectivity problems were observed when they both compete within the same molecule.¹⁴

We report here our contribution to the synthesis of Ar(Alk)BX family members with Ar = Mes. The methodology is based neither on an exchange reaction nor on the use of an alkyl-metal reagent as one might have been expected, but on the reaction of mesitylborane with vinylhalides that operates in a hydroboration/rearrangement sequence leading ultimately to a haloborane product. Standard reactivities of selected synthesized (aryl)(alkyl)(halo)boranes are also described, illustrating the potential of this simple synthesis methodology. In the continuity of the chemistry of stable monosubstituted boranes¹⁵ that we have been developing for some years,¹⁶ we were interested in the hydroboration reaction of vinyl halides. Although investigated with different hydroborating agents such as B₂H₆ or BH₃,¹⁷ diethylborane,¹⁸ 9-BBN¹⁹ or catecholborane,²⁰ this reaction remains unclear and difficult to rationalize with the outcome of the reaction strongly depending both on the substrate, on the hydroborating agent and on the reaction conditions. However, and based on the observations of Di Pasto^{17c, 17e} and Brown,^{17f, 19b} it appeared that hydroboration of vinyl halides might be a viable and

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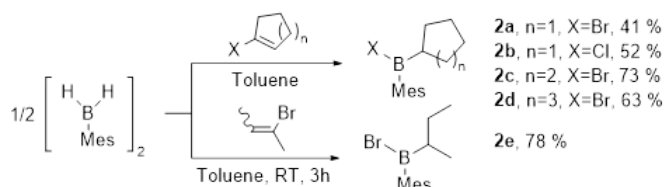
^b LPCNO, CNRS & INSA, Université de Toulouse, 135 avenue de Rangueil, 31077 Toulouse, France.† Electronic Supplementary Information (ESI) available: CCDC 2121188 (3a), 2121189 (4a), 2121190 (4c) and 2121191 (4d) contain the supplementary crystallographic data for this paper. They can be obtained free of charge from the Cambridge Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Experimental procedures, compounds characterization, DFT-calculations. See DOI: 10.1039/x0xx00000x

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simple synthetic strategy to obtain isolable (aryl)(alkyl)haloboranes.

Our previous results in the field of the B-H activation with mesitylborane **1**¹⁶ led us to select this monosubstituted hydroborating reagent as the best compromise between reactivity, stability and accessibility.²¹ A first reaction was performed under stoichiometric conditions with 1-bromocyclopentene in toluene at low temperature (-78 °C). Once warmed to room temperature and stirred for 1h, the ¹¹B{¹H} NMR spectrum of the reaction mixture revealed a clean reaction takes place with the complete disappearance of the starting mesitylborane dimer **1** (δ 22) and the almost exclusive presence of a low field shifted signal at δ 81. In the ¹¹B NMR spectrum, no direct *J*_{B-H} direct coupling could be detected excluding the presence of hydroborane species. After work-up, the boron compound was isolated as an oil in 41% yield. It was fully characterized by multinuclear NMR, mass spectroscopy and was unambiguously identified as the (mesityl)(cyclopentyl)bromoborane **2a** (scheme 1).



Scheme 1 Scope of the reaction of [MesBH₂]₂ with vinyl halides (isolated yields).

To extend the scope of the reaction for a viable application, the influence of the vinylic moiety was first evaluated under similar reaction conditions. With 1-bromocyclohexene, 1-bromocycloheptene and 2-bromo-but-2-ene (*Z/E* mixture), the reaction operates similarly and the corresponding cyclohexyl-, cycloheptyl- and (sec-butyl)(mesityl)bromoborane **2c-e** were isolated as oils in 73% (**2c**), 63% (**2d**) and 78% (**2e**) yield, respectively (scheme 1). In the case of 1-chlorocyclopentene, the reaction starts at RT and is completed after 13h at 60°C leading to the corresponding chloroborane **2b** isolated in 52% yield (scheme 1).

To go one step further, the reactive behaviour of representative (mesityl)(alkyl)bromoboranes was evaluated 1) for direct access to borocation species²² that have recently attracted considerable interest for new ionic liquids,²³ as multistep redox-active species²⁴ and materials²⁵ or anion receptors,²⁶ and 2) for the synthesis of 2-arylpyridine derived boron N⁺C-chelates driven by the recent interest for their photochemical behaviour and photophysical properties.²⁷ Upon reaction with 4,4'-dimethyl-2,2'-bipyridine in dichloromethane, **2a** and **2e** were converted into the corresponding boronium cations **3a** and **3e**, respectively (Figure 1). They were isolated in moderate to good yield and were fully characterized by HMRS and multinuclear NMR spectroscopy. Compared to their precursor **2a** (δ 81) and **2e** (δ 81), the ¹¹B{¹H} NMR spectra of **3a** and **3e** each show a broad, high-field shifted signal (Δδ 72 ppm) at δ 8.5 (**3a**) and 9.0 (**3e**) indicating the presence of a tetracoordinated and thus electronically saturated boron atom. The X-ray structure of **3a** was determined at 150K (Figure 1). The asymmetric unit

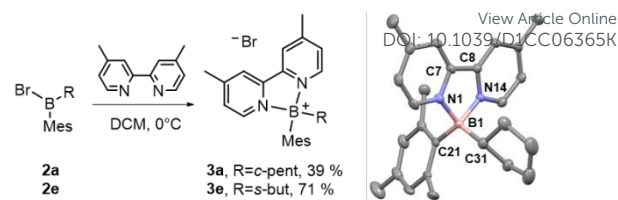
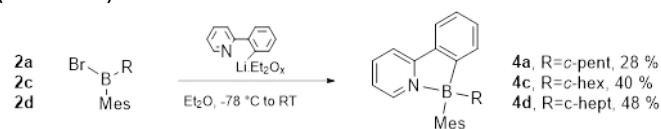


Figure 1 Left: representative synthesis of 2,2'-bipyridylboronium bromide **3** from bromoboranes **2**; Right: X-ray structure of **3a**. hydrogen atoms and bromide counter-anion are omitted for clarity. Selected bond lengths (Å) and angles (°): N1-B1 1.608(6), N14-B1 1.600(6), C21-B1 1.632(6), C31-B1 1.630(7); N14-B1-N1 94.60(3); C31-B1-C21 121.50(4).

contains four independent molecules with very similar geometrical features; one of these is discussed in the following. The boron atom is in a distorted tetrahedral environment. The bipy unit displays a nearly planar conformation with a NCCN torsion angle between both pyridyl rings of 4.30(5)°, an acute NBN angle of 96.40(3)° along with a large CBC angle of 121.50(4)°. CBC and NBN planes are nearly orthogonal (87.71°) as one would expect from a tetracoordinated boron cation. BN bond lengths (1.600(6) and 1.608(6) Å) are identical within experimental error and in the range of reported values for bipyridyl boronium structures^{24, 28} whereas B-C bond distances (1.630(7) and 1.632(6) Å) are found slightly longer.

As a representative reactivity, the reaction of **2a**, **2c** and **2d** with 2-(2'-lithiophenyl)pyridine was performed in Et₂O at low temperature leading to the corresponding boron N⁺C-chelates (Scheme 2).



Scheme 2 Synthesis of 2-phenylpyridine N⁺C boron chelates **4**.

They were isolated after work-up in 28% (**4a**), 40% (**4c**) and 48% (**4d**) isolated yield, respectively, and were fully characterized by HRMS and multinuclear NMR spectroscopy. In the ¹¹B NMR, they both exhibit a high field shifted signal at δ 3.5 (**4a**), δ 4.2 (**4c**) and δ 4.6 (**4d**), respectively, in agreement with the presence of a tetracoordinated sp³-hybridized boron within the molecule. The X-ray structures of **4a**, **4c** and **4d** were determined at 150K ascertaining the N⁺C-chelate connectivity with the boron atom (Figure 2).

Having demonstrated the synthetic potential of the hydroboration of vinyl halides with mesitylborane dimer and the versatility of the resulting (mesityl)(alkyl)haloboranes, we

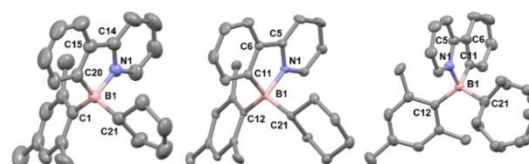


Figure 2 X-ray structure of **4a** (left), **4c** (middle) and **4d** (right). hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **4a**: N1-B1 1.634(2), C1-B1 1.640(2), C21-B1 1.650(2), C20-B1 1.613(2); N1-B1-C20 96.4(1); C1-B1-C21 118.0(1); C20-C15-C14-N1 2.1(2); **4c**: N1-B1 1.634(2), C11-B1 1.616(3), C21-B1 1.658(3), C12-B1 1.641(2); N1-B1-C11 96.1(1); C12-B1-C21 116.6(1); C11-C6-C5-N1 4.4(2); **4d**: N1-B1 1.634(3), C11-B1 1.615(3), C21-B1 1.658(9), C12-B1 1.649(3); N1-B1-C11 96.11(16); C12-B1-C21 117.30(4); N1-C5-C6-C11 0.4(3).

focused on the involved mechanism in the light of previously reported studies.^{17–20} Two related aspects were of particular interest, namely the regioselectivity of the hydroboration reaction with mesitylborane dimer and the stability of the resulting adducts leading to the formation of the B–Br bond in the isolated product. In order to better understand and unveil the mechanism of the reaction, a DFT study was carried out at the DFT-B3LYP-D3 level of theory.

As a model reaction, the reaction between mesitylborane and bromocyclopentene was computed as shown in the enthalpy (free enthalpy) profile in Figure 3. After the endothermic dissociation of the starting mesitylborane dimer (**A**) to give the monomeric species MesBH₂ in interaction with bromocyclopentene (+17.9 kcal.mol⁻¹), the second step involves the hydroboration (HB) of the alkene with two possible regioselectivities relative to bromine: either *pathway 1* with the boron approaching the α -carbon of the olefin (α -HB) or *pathway 2* with the boron approaching the β -carbon of the olefin (β -HB) (Figure 3). For *pathway 1*, the α -HB results in a syn-addition involving a transition state (**TS-B1C1**) located at 24.8 kcal.mol⁻¹ with respect to the reactants (**A**), and 6.9 kcal.mol⁻¹ with respect to adduct **B1**. The transition state consists in an unsymmetrical alkene-borane π -complex (B–C1 1.871 Å, B–C2 1.933 Å) developing an interaction between an elongated B–H2 bond (1.221 Å versus 1.197 Å in free MesBH₂)^{16a} and the β -carbon (see S.I. Figure S1-DFT for the computed bond lengths, Table S1- and S2-DFT for the Wiberg indexes and NPA charges and Figure S2-DFT for the molecular orbitals). Via the one-step formation of the C ^{α} –B and C ^{β} –H bonds, the hydroboration reaction leads to the α -halogenated alkylborane compound **C1**, located at -4.6 kcal.mol⁻¹ relative to **A**. Compound **C1** may then undertake a concerted intramolecular exchange between the C–Br halogen atom and the B–H hydrogen atom to afford the final compound **P**. The process involves a late transition state (**TS-C1P**) with a sp²-hybridized C ^{α} cyclopentyl carbon atom connected to the B centre set in a tetrahedral arrangement which is reminiscent of a type-I dyotropic rearrangement.²⁹ The interaction between the σ -BH orbital and the p orbital of the planar C ^{α} carbon is clearly observable in the HOMO-5 orbital of **TS-C1P** (S.I. Figure S4-DFT). For the alternative *pathway 2*, the β -HB

syn-addition presents similar features to those of the α -HB one with *i*) a comparable barrier (**TS-B2C2**) of 25.7 kcal.mol⁻¹ (vs 24.8 kcal.mol⁻¹ for α -HB) relative to **A** and 7.8 kcal.mol⁻¹ (vs 6.9 kcal.mol⁻¹ for α -HB) relative to **B2** and, *ii*) a resulting β -halogenated alkylborane **C2** lying at -2.6 kcal.mol⁻¹ relative to **A** (vs -4.6 kcal.mol⁻¹ for **C1** in the α -HB route). At that stage, the evolution of the HB product of *pathway 2* differs drastically from that of *pathway 1* since it involves an E_i elimination/hydroboration sequence to produce the final compound **P**. The E_i elimination is exothermic by 8.4 kcal.mol⁻¹ and leads to the halogeno(mesityl)borane and cyclopentene products (**D2**). It involves an activation barrier of 31.7 kcal.mol⁻¹ (**TS-C2D2**) which is in kinetic competition with the **C2** → **B2** back reaction at RT (31.7 vs 28.3 kcal.mol⁻¹). The ensuing HB reaction of cyclopentene with MesB(H)(Br) is strongly exothermic (-22.2 kcal.mol⁻¹) displaying a low activation barrier of 7.6 kcal.mol⁻¹ (**TS-D2P**). In the end, *pathway 1* and *2* are both formally accessible at RT although *pathway 1* is globally more kinetically favoured. The computed reaction between mesitylborane and chlorocyclopentene gives rise to similar energetic profiles (see S.I. S9-DFT) with *pathway 2* requiring more elevated temperature to operate due to a 3.3 kcal.mol⁻¹ higher energy barrier of **TS-C2D2** and a **C2** → **B2** back reaction more kinetically favoured than the E_i elimination process (28.0 vs 35.0 kcal.mol⁻¹). This is in line with the NMR monitoring of the reaction between [MesBH₂]₂ and chlorocyclopentene that shows the formation of the (mesityl)(alkyl)chloroborane from RT with completion of the reaction reached only after hours at 60 °C. It is reasonable to think that borane **C2**, once formed at RT, may either go back to the reagents **A** to engage in *pathway 1* or overcome the barrier of **TS-C2D2** if enough heating is provided to the system.

As a conclusion, hydroboration reaction of vinyl halides with MesBH₂ represents a direct and viable access to isolable (mesityl)(alkyl)haloboranes as valuable synthetic reagents. DFT-calculations clarify the speculated two-pathway mechanism showing that although *pathway 1* is more kinetically favoured, *pathway 2* is also accessible, at RT for Br and at higher temperatures for Cl. This work was performed using HPC resources from CALMIP (Grant 2017-[p17010]).

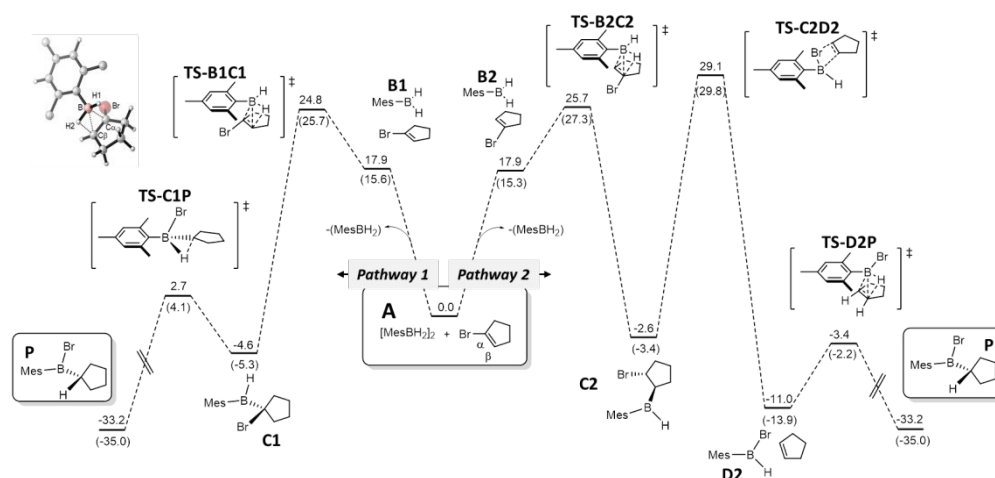


Figure 3 DFT computed enthalpy (free enthalpy) profile (in kcal/mol) of the reaction between MesBH₂ and c-pent-Br at the B3LYP-D3/6-31G(d,p) level of theory. *Pathway 1* and *2* from α - and β -hydroboration, respectively, are given.

Conflicts of interest

There are no conflicts to declare

Notes and references

§ The authors dedicate this publication to Professors Francesc Teixidor and Clara Viñas on the occasion of their birthday and in appreciation of their many years contribution to the boron cluster chemistry.

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