



Metal-Ligand Cooperation in Borenium Catalyst

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Abstract

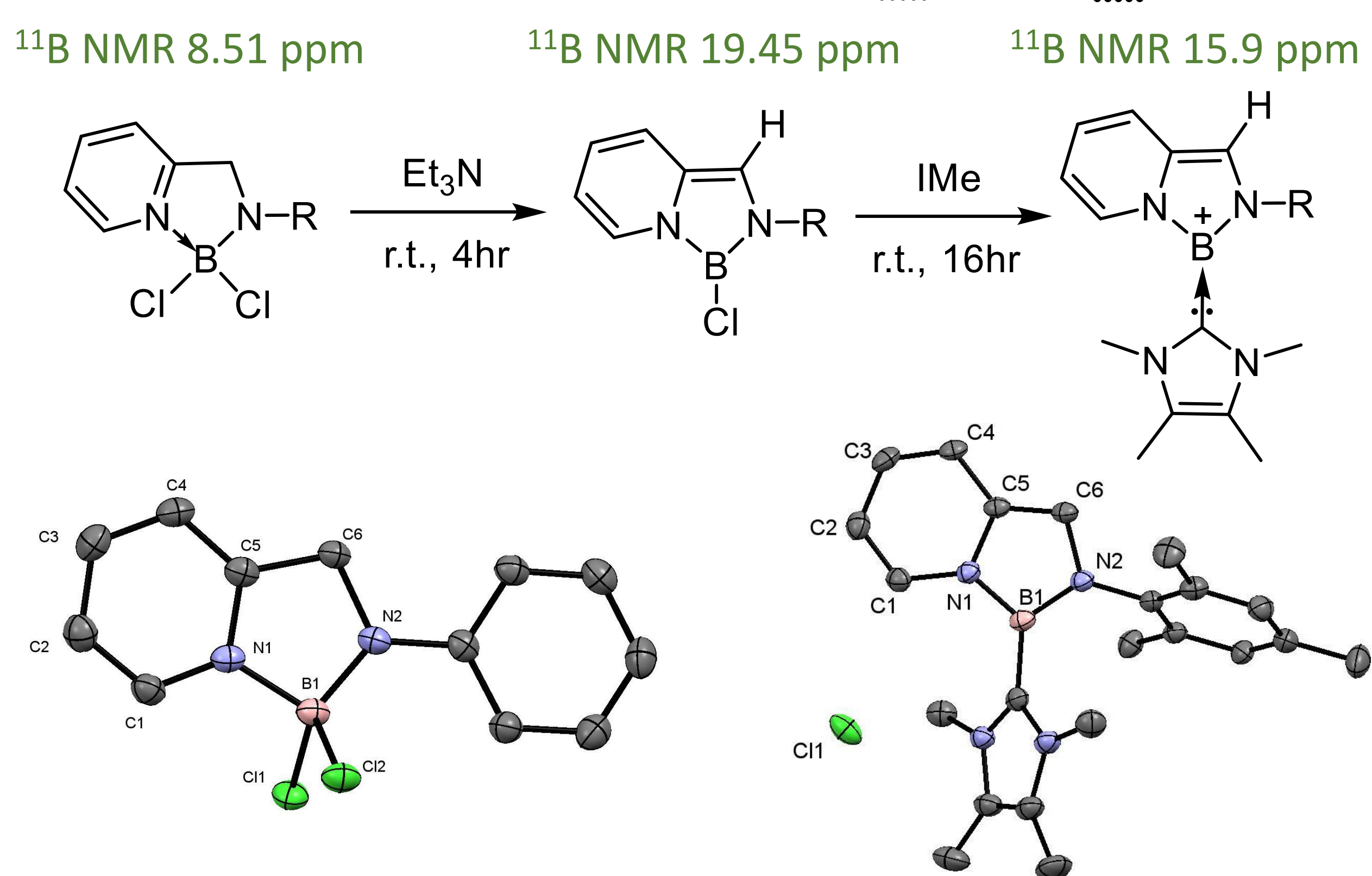
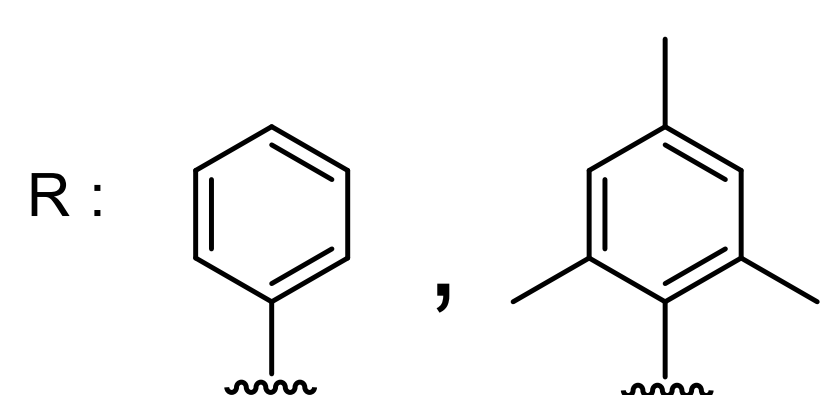
The combination of boron and non-innocent ligand has been explored by Milstein in 2016.¹ However, no catalytic reaction has been achieved with such boron-ligand cooperation interaction. In this work, we report a stable borenium cation featuring a non-innocent ligand that can cooperatively activate C=O double bond and amine-borane. The synthesis and reactivity of the borenium cation will be discussed.

Introduction

The combination of non-innocent ligand and transition metal has resulted in a lot of important breakthroughs in transition metal based catalysts. While some of the non-innocent ligands participate in electron transfer process, some are involved in activation of substrates with metal center cooperatively. Although the strategy has led to great success in d-block metals, the incorporation of non-innocent ligand to main group complexes has less developed. In the past few years, tricoordinate boron cation, borenium cation has received a lot of attention because of its potential application in catalytic hydrosilylation and hydrogenation.^{2,3} Since the borenium cation is too reactive, most of the works use bulky ligands like 2,6-lutidine and sterically demanding NHCs, and bulky substituents like mesityl and cyclopentadienyl to protect the boron center kinetically. Here we present another way to prepare catalytically active borenium center by placing the boron center in an aromatic ring generated from non-innocent ligand.

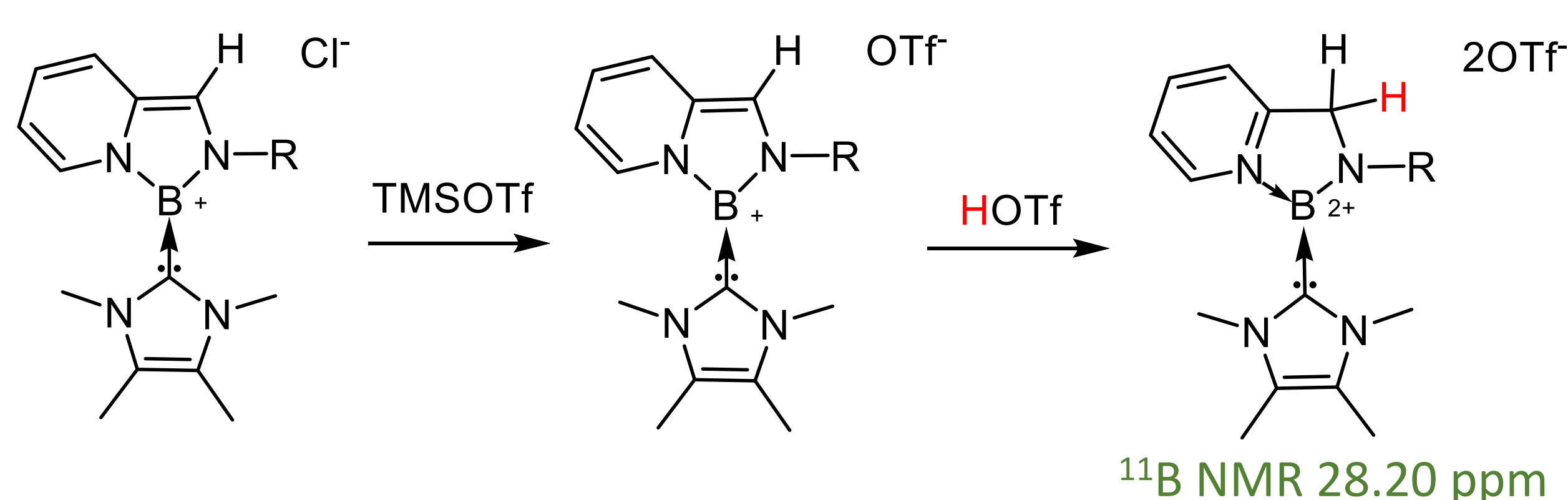
Results

Synthesis

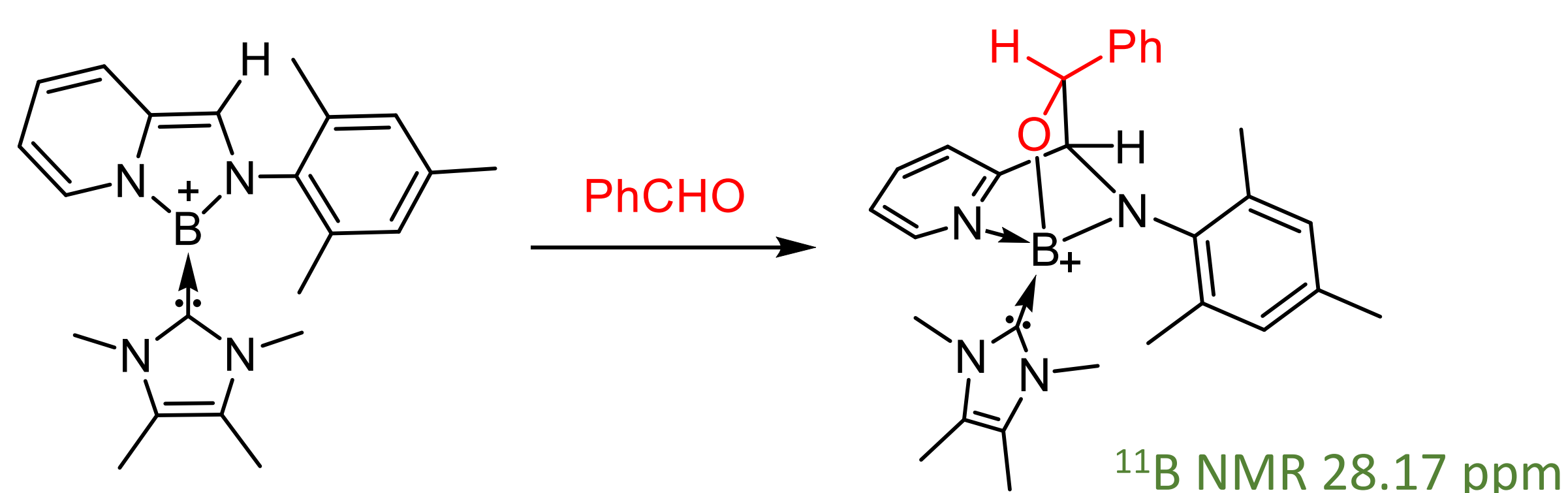


Bond length(Å)	Boron	Borenium
N1-C1	1.35	1.40
C1-C2	1.36	1.35
C2-C3	1.39	1.43
C3-C4	1.38	1.35
C4-C5	1.38	1.44
C5-N1	1.34	1.42
C5-C6	1.49	1.35

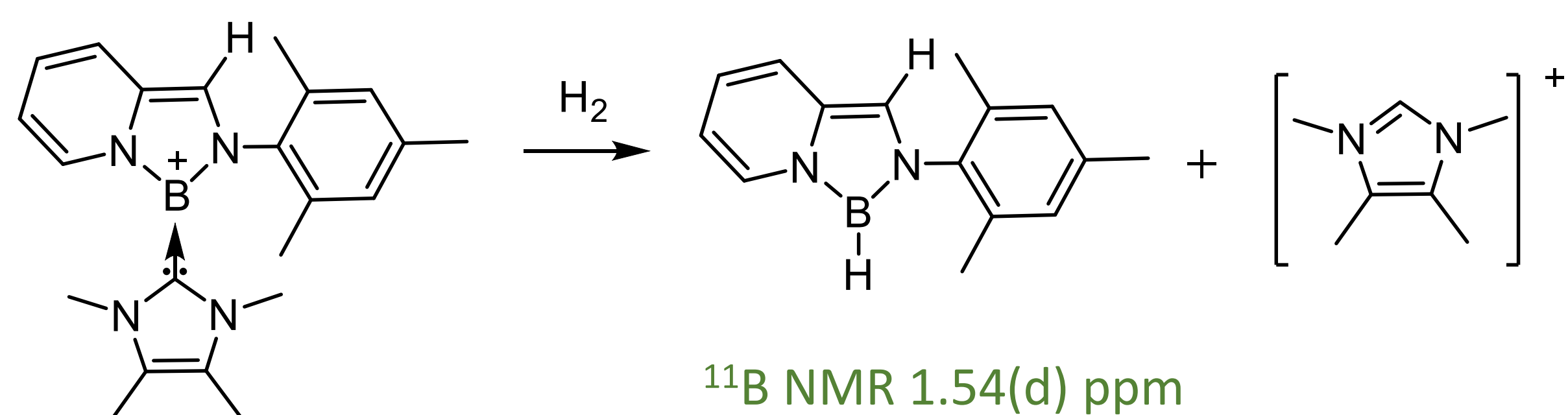
Borane Dication



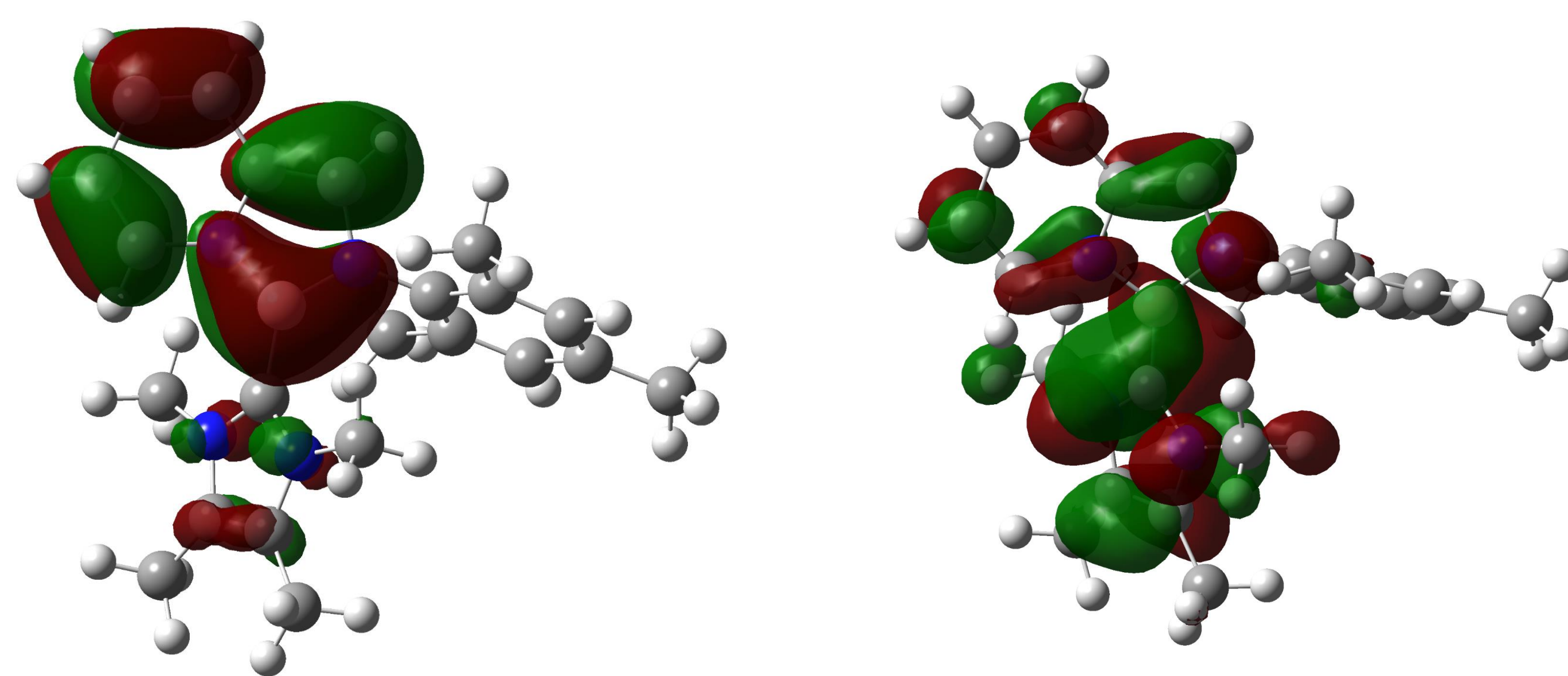
Reactivity toward Aldehyde



Reactivity toward H₂

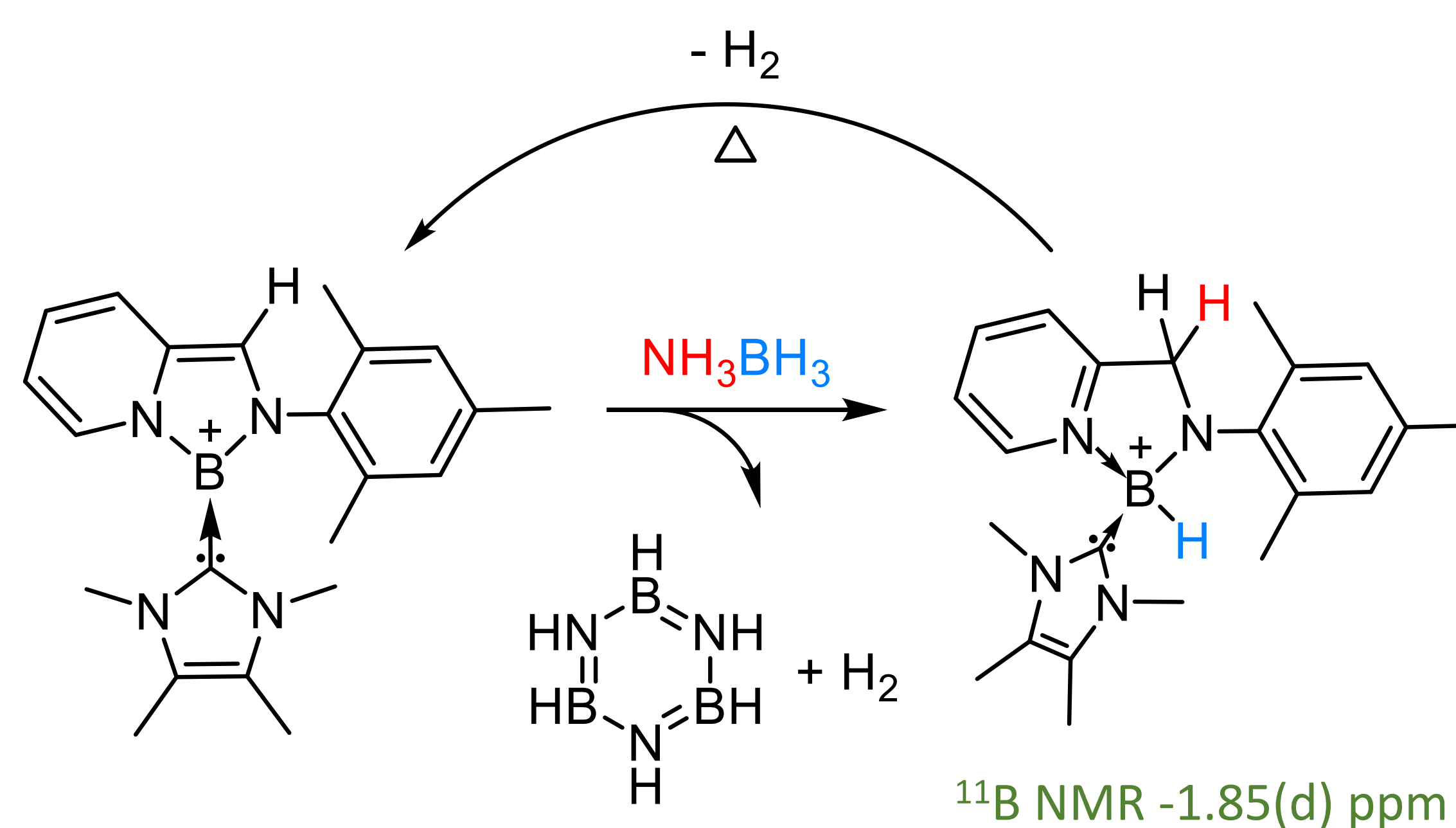


Theoretical calculation



Computed HOMO & LUMO

Amine-Borane dehydrogenation



Conclusion

A non-innocent ligand supported borenium cation has been successfully synthesized and its structure has been characterized by crystal data. Protonation of the borenium cation took place at the ligand led to a tricoordinate boron dication which might have some reaction potential. Although the borenium complex is not able to catalyze hydrosilylation of benzaldehyde and decomposes slowly under H₂, the non-innocent ligand and boron center cooperatively promote the dehydrogenation of amine-borane at room temperature. The resulting boronium cation can be heated to 60 °C to regenerate the original borenium cation.

References

1. U. Gellrich, D. P. Yael, L. J. W. Shimon, and D. Milstein, *J. Am. Chem. Soc.*, **2016**, *138*, 13307.
2. S. E. Denmark* and Y. Ueki, *Organometallics*, **2013**, *32*, 6631.
3. J. M. Farrell, J. A. Hatnean, and D. W. Stephan, *J. Am. Chem. Soc.*, **2012**, *134*, 15728.