

N-borane substituted N-heterocyclic carbenes for small-molecule activation

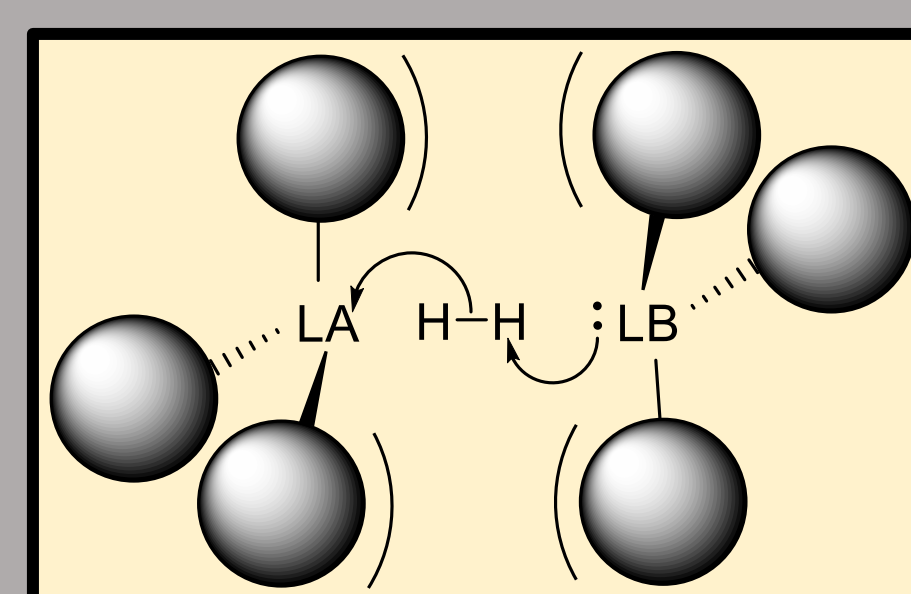
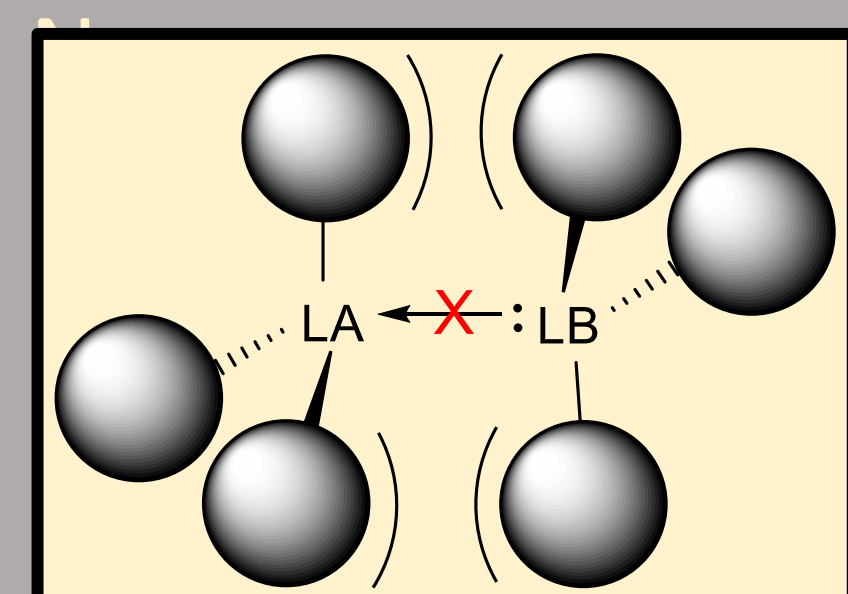


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Abstract

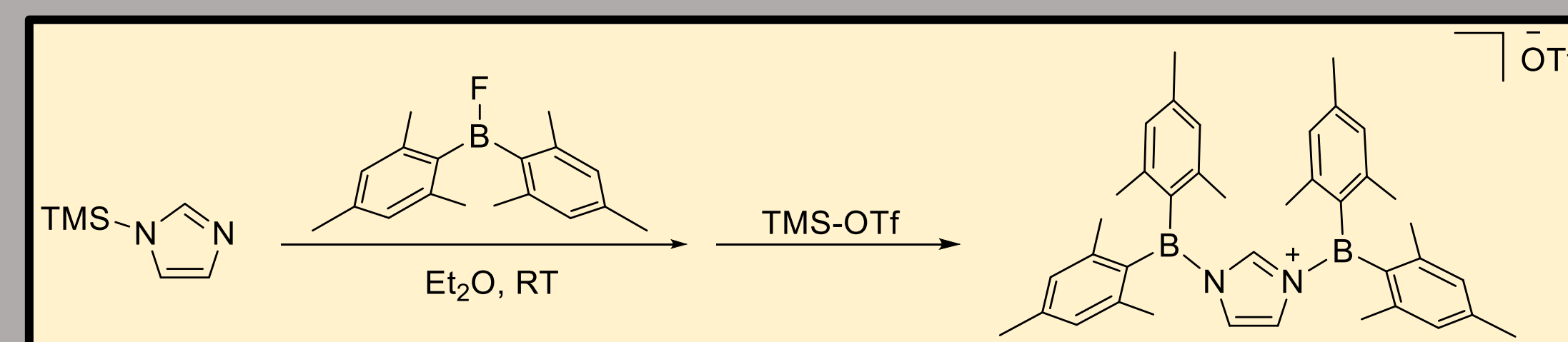
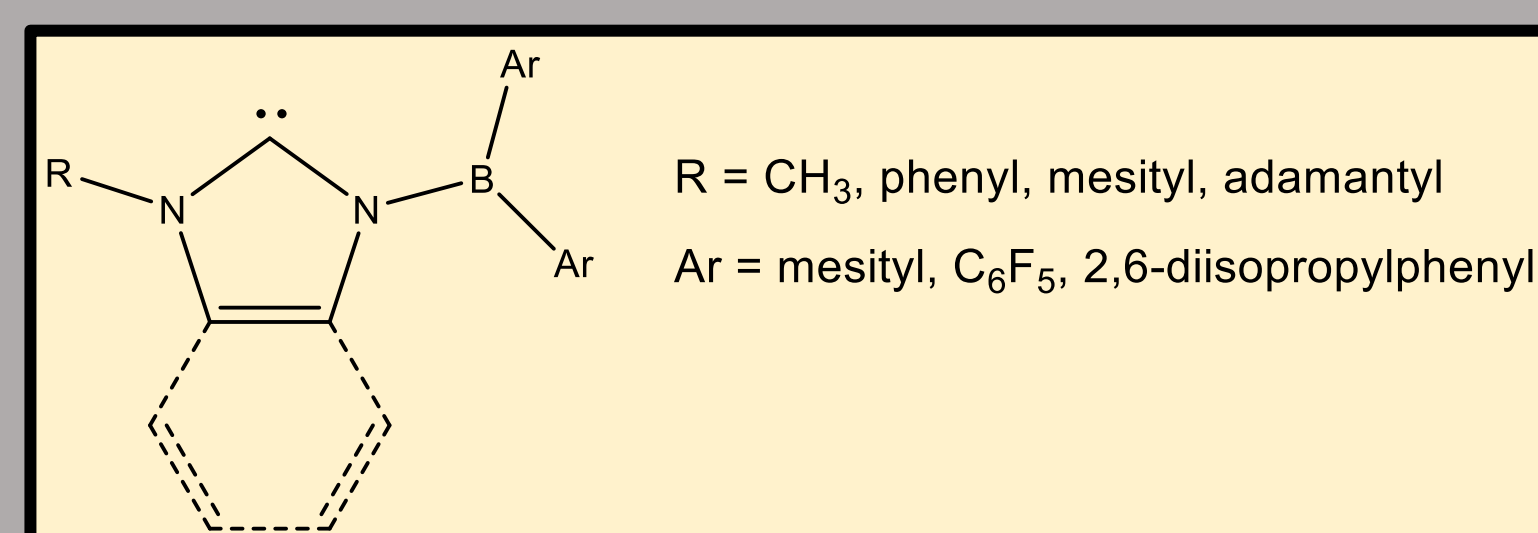
The effect of greenhouse gases on the environment has created a clear need for direct chemical activation and atmospheric removal of these gases. CO₂'s particular stability (due to it containing carbon in its highest oxidation state) has made it the subject of many small-molecule activation studies. Additionally, hydrogenation and nitrogen fixation are resource and energy-intensive processes that require the splitting of H₂ and N₂, respectfully. Methods for splitting or activating all three of these small molecules typically rely on transition metal catalysts, but the development of metal-free methods is promising financially, energetically, and in terms of safety of the catalysts. Since 2006, Frustrated Lewis Pairs-- combinations of Lewis acid and base that are unable to form adducts due to their steric bulk--have proved to be capable of H₂ and CO₂ activation by polarizing them and acting upon them in a concerted manner¹. This project seeks to synthesize a series of N-borane substituted



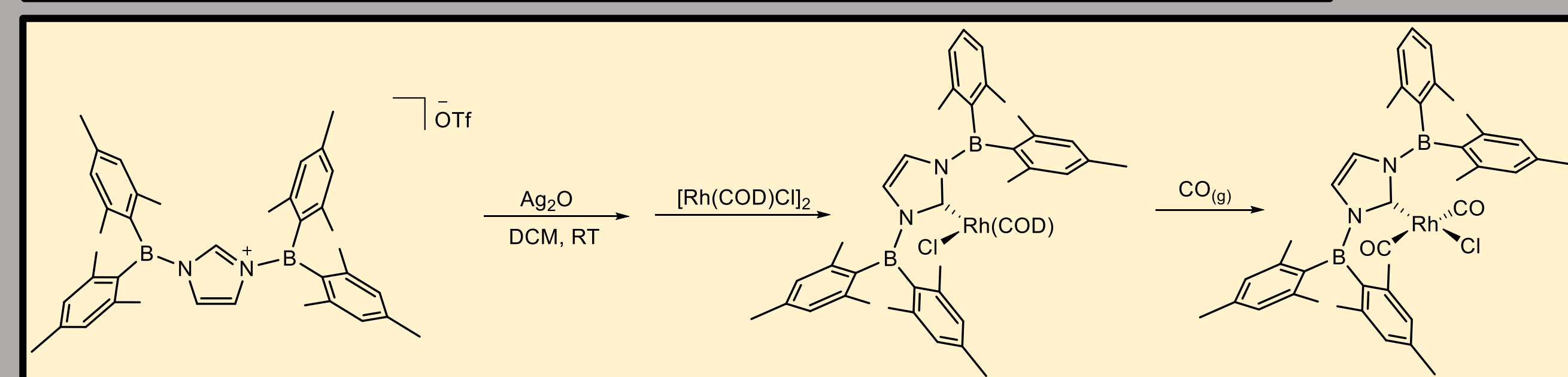
heterocyclic carbenes with the potential to act as intramolecular FLP. The bulk of the borane centers expected to make a more kinetically stable carbene, and they will potentially act as tunable groups to change the structures' properties, both as FLPs and as ligands for transition metal catalysts.

Synthesis and Preliminary Results

We are working to synthesize a series of bi- and monosubstituted imidazol-2-ylidene and benzyimidazol-2-ylidenes of the general structure shown to the right.



Synthesis of imidazolium salt precursor². 1-methyl-3-[B(Mes)₂]imidazolium triflate has also been made.

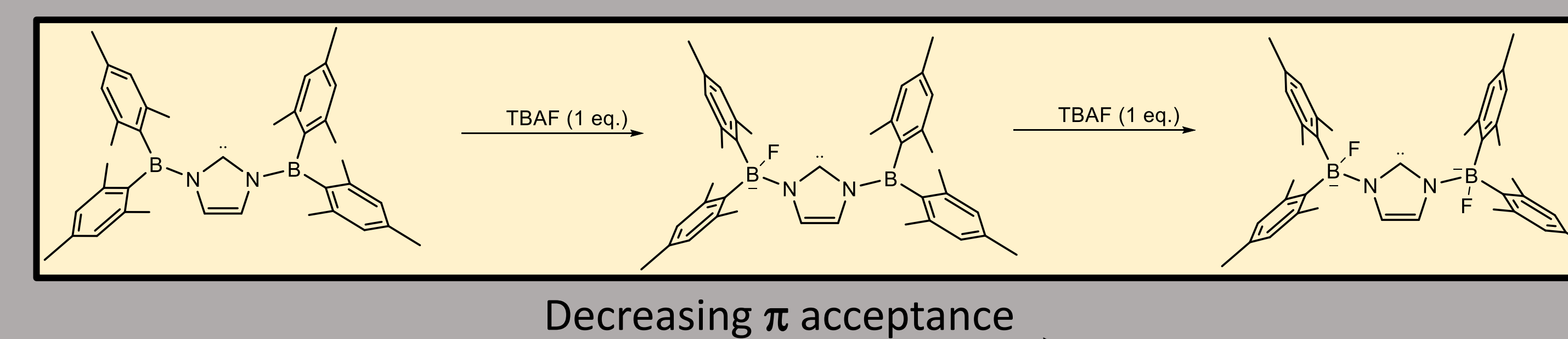
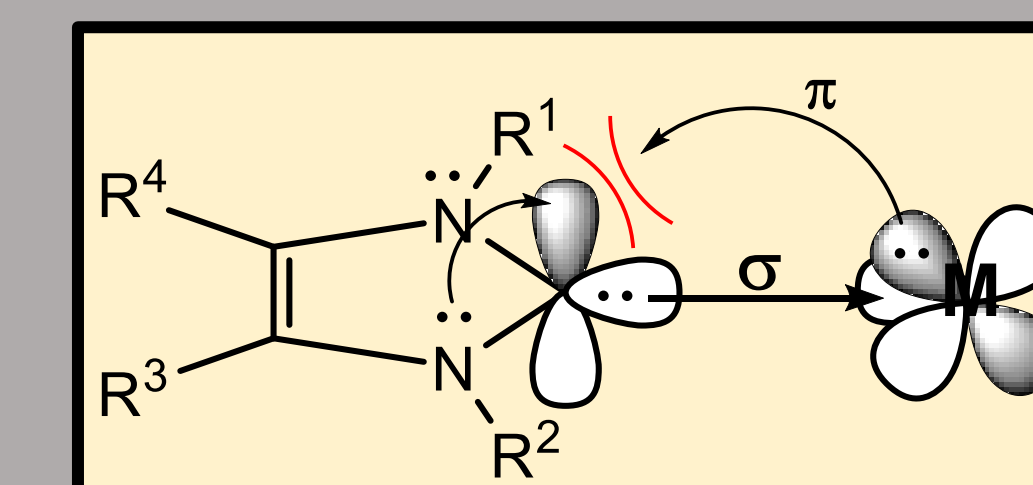


Synthesis of corresponding Rh(CO)₂(NHC)Cl complex³. Also carried out with 1-methyl analog mentioned above.

Conclusions and Future Experiments

Characterization and crystallization of Rh complexes of the mono and diborane-substituted NHC is underway, as is synthesis of the bulkier imidazoles identified in the computational study as having the potential to form stable carbenes. Deprotonation of the imidazolium salts needs to be done to produce the free carbenes and observe their reactivity with small molecules, beginning with H₂.

To achieve our goal of structure tuning, one and two equivalents of fluoride will be added to the borane centers of both the free carbene and ligand to observe the steric and electronic changes this causes. Currently the plan is to do this with TBAF, as it is an organic-soluble F⁻ source. We hypothesize that this will decrease the π-accepting ability of the ligands.

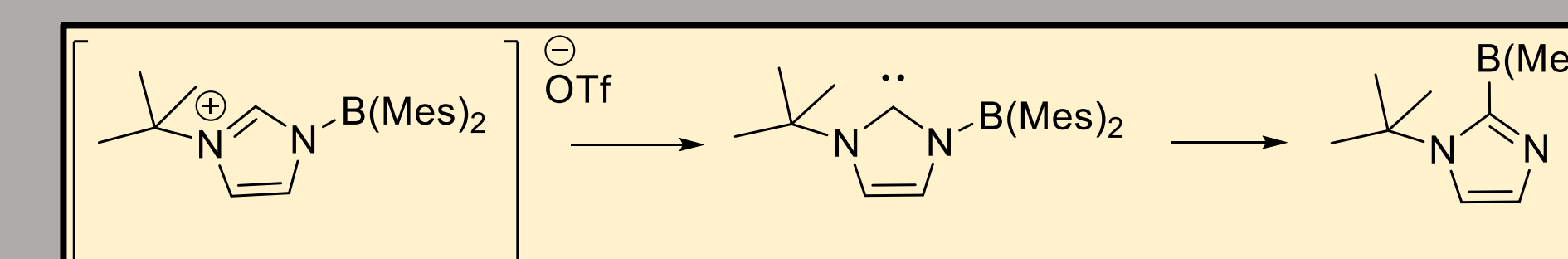


GOAL:

Create borane-carbene intramolecular Frustrated Lewis Pairs that can also function as tunable ligands for transition metal catalysis

Computational Work

Inspired by the experimental finding by Liu et al.⁴ that B(Mes)₂ migrated to the carbene upon deprotonation of the imidazolium salt, a computational study is underway to assess how large the other N-substituent needs to be to prevent this migration.



Through DFT, ωB97X-D functional, and 6-31G* basis set, energy of carbenes and their migrated products have been calculated to see which migrations are energetically unfavorable. Preliminary data suggests N-phenyl, mesityl, diisopropylphenyl, adamantyl, and B(Dipp)₂ substituted imidazoles may need to be synthesized to prevent migration. Energy of a possible 1,2 borane shift and diradical intermediate are also being investigated to further aid in carbene design.

References

- 1) W. Stephan, D.; Erker, G. *Angew. Chem. Int. Ed.*, 2015, 54, 6400–6441.
- 2) Synthesis adapted from: Herrmann, W. A.; Köcher, C.; Gooßen, L. J.; Artus, G. R. J. *A European Journal*, 1996, 2 (12), 1627–1636.
- 3) Synthesis adapted from: Mata, J.; Chianese, A.; Miecznikowski, J.; Poyatos, M.; Peris, E.; Faller, J.; Crabtree, R. *Organometallics*, 2004, 23, 1253–1263.

- 4) Liu, W.; Liu, Y.; Lin, T.; Peng, S.; Chiu, C. *Inorg. Chem.* 2017, 56, 10543–10548.

Acknowledgements

- Caputo Group
- Gonghu Li and Roy Planalp groups
- University of New Hampshire Department of Chemistry