The Synthesis of N-Heterocyclic Carbene Ligands for Transition Metal Catalysis

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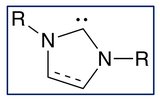
Abstract

N-Heterocyclic Carbenes (NHCs) are widely used as ligands for transition metal catalysis because of its ability to donate a lone pair of electrons, creating a a very strong bond with a metal center. This strong ability to bond stems from the aromaticity of the heterocyclic ring, stabilizing the empty p-orbital on the carbon. The versatility of the NHC structure and the tunability of its steric and electronic structure is what sets this class of metal ligands aside from its predecessors. The synthesis of different substituents bound to the nitrogen groups have large effects on the overall stability of the ligand, and electronics of the carbene itself.

Carbene Electronics

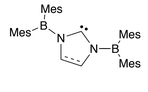
Important Features of the NHC

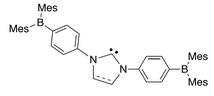


- *Aromaticity of the heterocyclic ring*
- *Tunability at nitrogen groups*
- ***Steric Bulk on ligand** = Stability*
- ***Electron withdrawing substituents** = Reactive*

Our Idea;

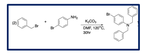
- *Boron easily accepts π-electrons due to empty p-orbital, making it a strong electron withdrawing group.*
- *This feature as well as the direct N-B bond makes it subject to **nucleophilic attack***
- *A **bulky, aryl 'spacer'** between the boron and nitrogen protect this boron from nucleophilic attack, **due to the strength of C-B bond vs. B-N bond***
- ***Comparison** of previously made NHC in Caputo group (left) with the proposed product of this synthesis (right) below;*





N,N-dibenzyl-4-bromoaniline

- **First Successful Attempt** (left): Green/yellow oil that formed **white crystals** overnight (crystal image below)



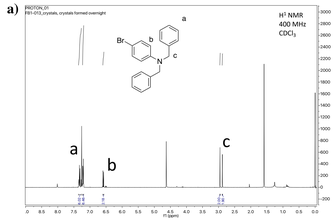
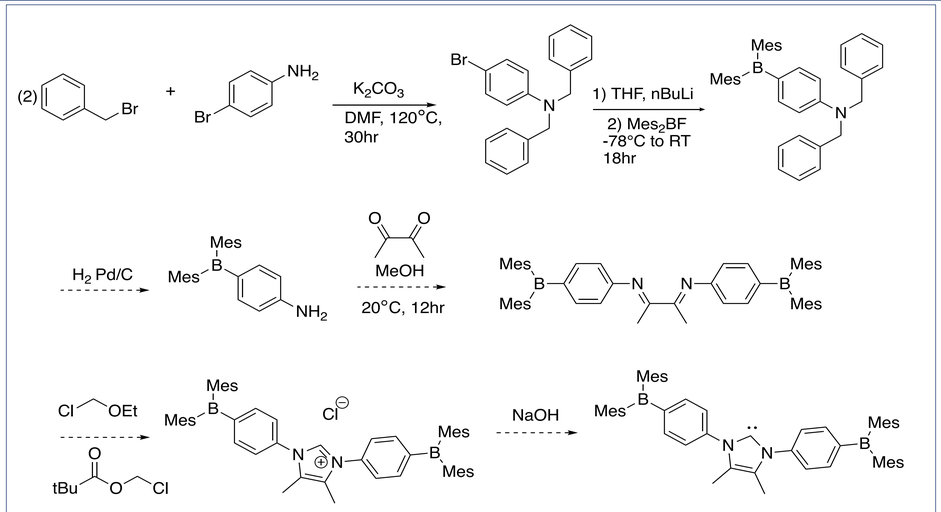


Figure 4. **a)** ^{1}HNMR data for FB013 crystals, clear integration. **b)** Image of crystal via X-Ray CrystallographyI .

Proposed Synthetic Route



N,N-dibenzyl-4-(dimesitylboryl)aniline

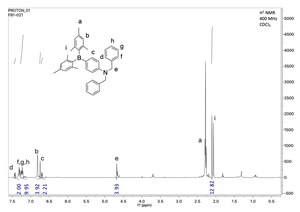


Figure 1. Successful synthesis of N,N-dibenzyl-4-(dimesitylboryl)aniline, low yield.

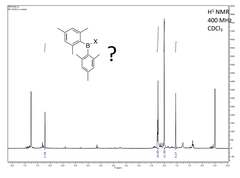


Figure 2. Unsuccessful synthesis ofN,N-dibenzyl-4-(dimesitylboryl)aniline. Possible hydrolysis of Boron group.

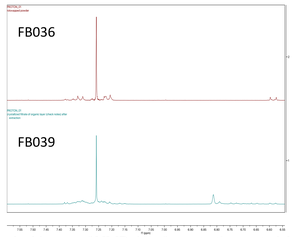
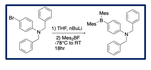
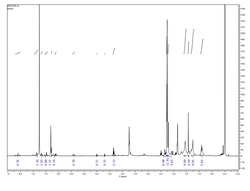


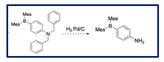
Figure 3. Stacked image of NMR data from starting material to product. *FB036* is the N,N-dibenzyl-4-bromoaniline. *FB039* should be the N,N-dibenzyl-4-(dimesitylboryl)aniline, but it was uncertain.

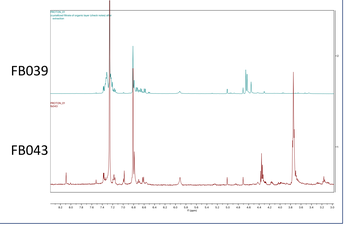


Hydrogenation of N,N-dibenzyl-4-(dimesitylboryl)aniline



- **FB043**
- Ninhydrin stain of TLC shows **no amine**
- Did water interfere? More analysis is needed.





Future Project Goals

N,N-dibenzyl-4-(dimesitylboryl)aniline Reaction Step

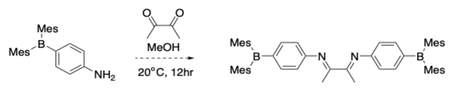
- Need to optimize reaction in order to increase yield
  - *Keep out H_2O to prevent hydrolysis of boron group*
- Better NMR data to fully analyze

Failed FB043 Reaction Step

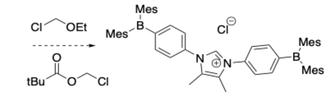
- NMR Analysis
  - *Benzyl peaks still present = no cleavage of benzyl groups*
  - *Aliphatic region = same, Aromatic region =shifted*
- Possible outcomes;
  - *Dimerization*
  - *Starting material present*

Conclusions

- Improve hydrogenation reaction
- **Optimizing Future Reaction Steps;**
  - After Hydrogenation:



  - Imidazolium Salt Formation:



- After the imidazolium salt has been formed, the last reaction step is to treat the product with NaOH in order to get the catalytic form of the NHC.

Acknowledgements

I would like to thank Dr. Christine Caputo and Zane Relethford, as well as everyone in the Caputo group, for assisting me with learning and offering advice on the reactions in this synthesis. I would also like to thank the Berda group, as well as the Li group for providing the chemicals needed to complete some reactions within the synthetic route.

References

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