Expanding on the Synthesis of Imidazolium-Based NHC Ligands

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Introduction

N-heterocyclic carbenes (NHCs) are a convincing choice for building ligands in transition metal complexes. In general, carbenes are neutral compounds containing a divalent carbon atom possessing a lone pair in an sp2 hybridized orbital that is available for coordination. A contributing factor to the NHCs' efficacy is that they are stabilized through electronics and are effective sigma donors, forming strong bonds with transition metals. This stabilization is attributed to the two nitrogen atoms 'pulling' electron density away from the usually reactive carbene carbon. Supplementally, the lone pairs of electrons on the nitrogen atoms can delocalize and 'push' into the vacant p orbital of the carbene center, thus stabilizing the singlet carbene. Imidazolium can serve as a backbone for NHCs, allowing for nearly infinitely diverse functionalization options, namely, variation of the N-substituents. Ligand synthesis trials previously conducted for this project indicated that a ligand built with a methyl substituent was the most successful, given the small size of the methyl group. These ligand precursors were used to construct a bimetallic Au-Cu complex to study metallophilic interactions, which are unusual, attractive interactions between closed-shell metal atoms. This type of interaction is the driving force behind some unique photophysical properties of this class of molecules.

Design and Rationale

Imidazolium-based ligands were selected for this project because of the diversity of N-substituents that can be investigated. However, the previous synthetic routes explored for this project involved the initial isolation of an ammonium phosphate salt, followed by similar reaction conditions to those established by the Debus–Radziszewski imidazole synthesis. This method was simplified into a one-pot method, which was advantageous for synthesizing many ligands with varying N-substituted R groups. While one-pot synthesis methods are attractive for developing a library of the same type of ligand with differing N-substituents, the yield and isolation of the final product prompted the exploration of an improved route. An alternative synthetic method to improve the final product yield was investigated, which would provide an easier pathway to the bimetallic species. Another factor that influenced the design of a new synthetic route was a recent decision by the United States Environmental Protection Agency stating dichloromethane presents an unreasonable risk to human health and, thus, should be removed from any academic laboratories.

Design and Rationale

Dichloromethane is a common solvent used in many laboratory applications because of its ability to dissolve a wide range of organic compounds. The previously used synthetic route employed dichloromethane as a key solvent for multiple steps of the synthesis. This new ruling served as the catalyst to explore new routes involving more benign solvents.

Results and Discussion

The synthetic pathway that proved the most advantageous involved deprotonating the 2-picolyl chloride hydrochloride with sodium bicarbonate as an initial step. The reaction pathway can be seen in **Figure 1**.

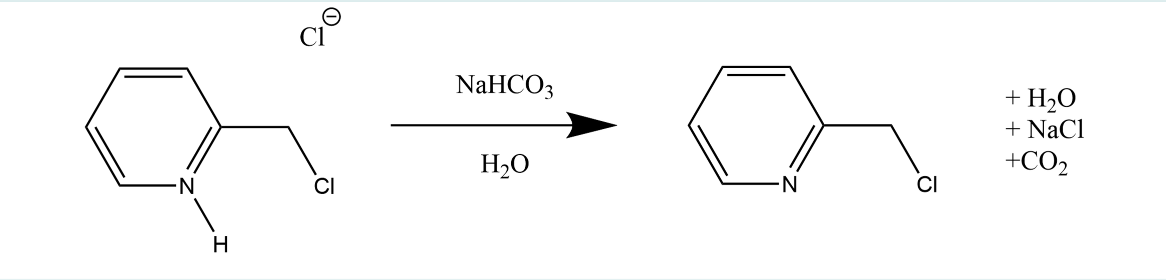

Figure 1: Deprotonation of 2-picolyl chloride hydrochloride by sodium bicarbonate

The product of this reaction was refluxed with 1-methylimidazole and sodium iodide in toluene. This allows 2-picolyl chloride to add a pendant pyridyl arm as another substituent of 1-methylimidazole, yielding the disubstituted imidazolium salt. This updated version of the ligand synthesis takes advantage of the Finkelstein reaction, which utilizes an S_N2 mechanism to substitute the chloride leaving group on 2-picolyl chloride to iodide, which functions as a better leaving group. The reaction pathway is detailed in **Figure 2.**

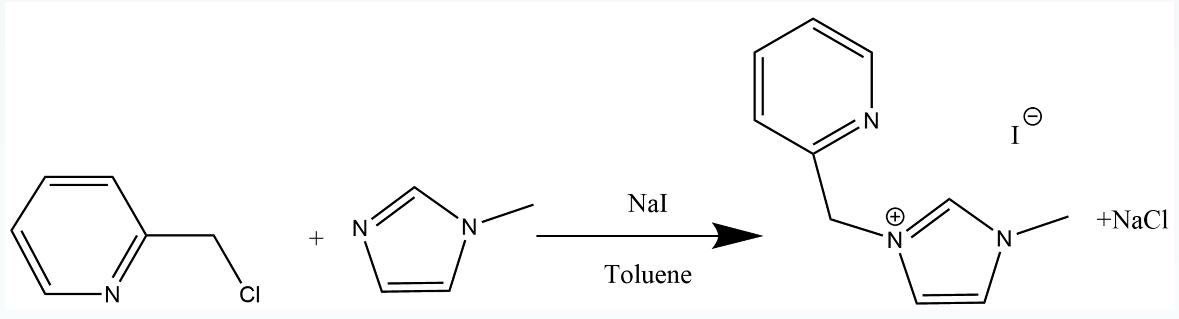

Figure 2: Finkelstein reaction on 2-picolyl chloride to add a pendant pyridyl arm onto imidazole backbone

This product then goes through an anion exchange reaction with potassium hexafluorophosphate, which also purifies the product. Once the final methylimidazolium-based ligand has been isolated, it will be used in a 4:1 ratio with Ag_2O to generate a monometallic silver(I) complex containing two NHCs.

Results and Discussion

This silver species will undergo a transmetallation reaction with Au(tht)Cl, yielding the monometallic gold species. The reaction pathway for this metallation can be seen in **Figure 3**.

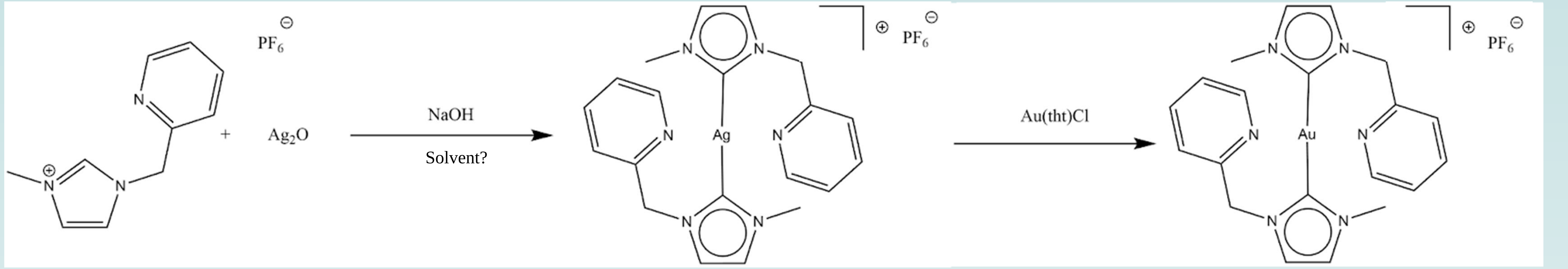

Figure 3: Proposed metallation and transmetallation reactions using 1-Methyl-3-(2-picolyl) Imidazolium hexafluorophosphate

Once the Au species is characterized, an equivalent of copper(I) will be added to generate a heterobimetallic species. An attempt at this reaction pathway utilized chloroform as a substitute to dichloromethane, which performed as expected until the primary metallation step. To avoid unfavorable reactions between chloroform and Ag_2O, it is pertinent to investigate another solvent system.

Conclusion

A new synthetic route for the methylimidazole-based ligands was developed, and improved product yield and isolation were seen. NMR spectra for 1-methyl-3-(2-picolyl) Imidazolium hexafluorophosphate was analyzed, and it was confirmed that the new synthetic pathway is successful. The final structure and NMR can be seen in **Figure 4.** Moving forward, different solvents will be explored to avoid the use of chloroform in the presence of Ag_2O to avoid any unfavorable reactions. A previous iteration of the 1-methyl-3-(2-picolyl) imidazolium hexafluorophosphate ligand was successfully used in the coordinated heterobimetallic Au-Cu system. After the finalization of the new solvent system for the updated synthesis, the photophysical properties of the heterobimetallic species will be investigated as a function of solvent coordination at the metal centers.

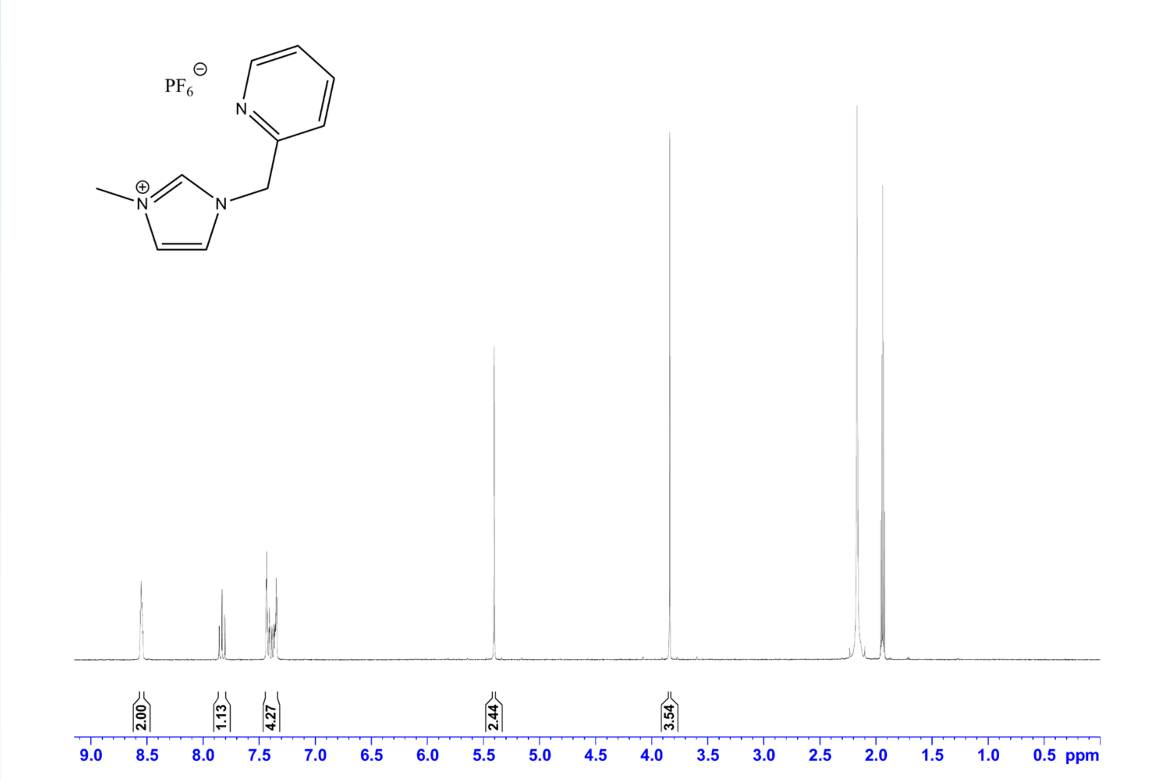

Figure 4: Structure and NMR of 1-Methyl-3-(2-picolyl) Imidazolium hexafluorophosphate

References

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