Synthesis of an *N*-Heterocyclic Phosphenium Gold Complex

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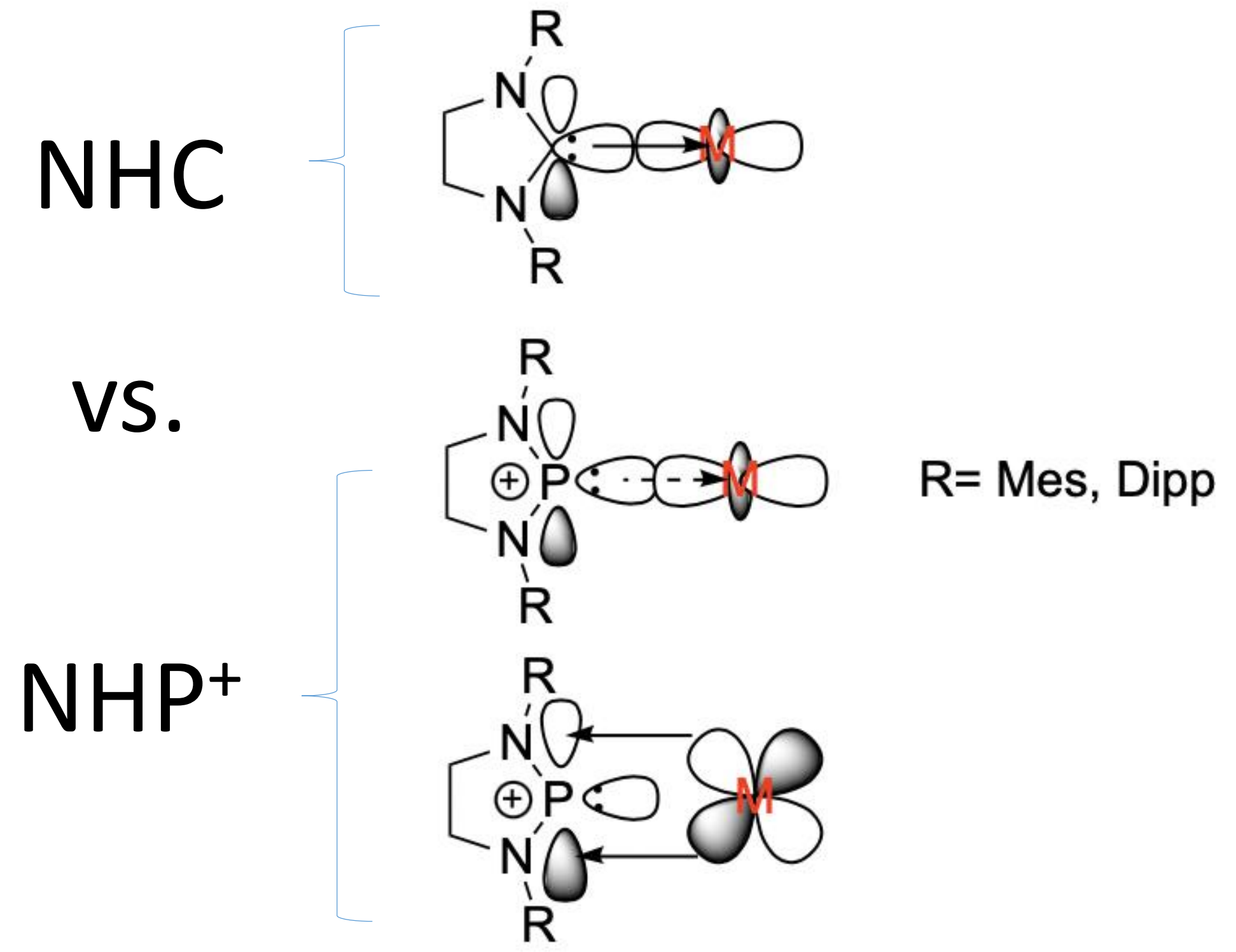
Introduction

N-Heterocyclic phosphenium cations (NHPs) are ligands that are much alike their more popular counterpart, *N*-heterocyclic carbenes (NHCs). NHCs have been used to make metal-NHC complexes that have been successful catalysts.

NHPs, on the other hand, have seen little use in catalytic applications, likely due to air and moisture sensitivity and the need to handle them under an inert atmosphere.



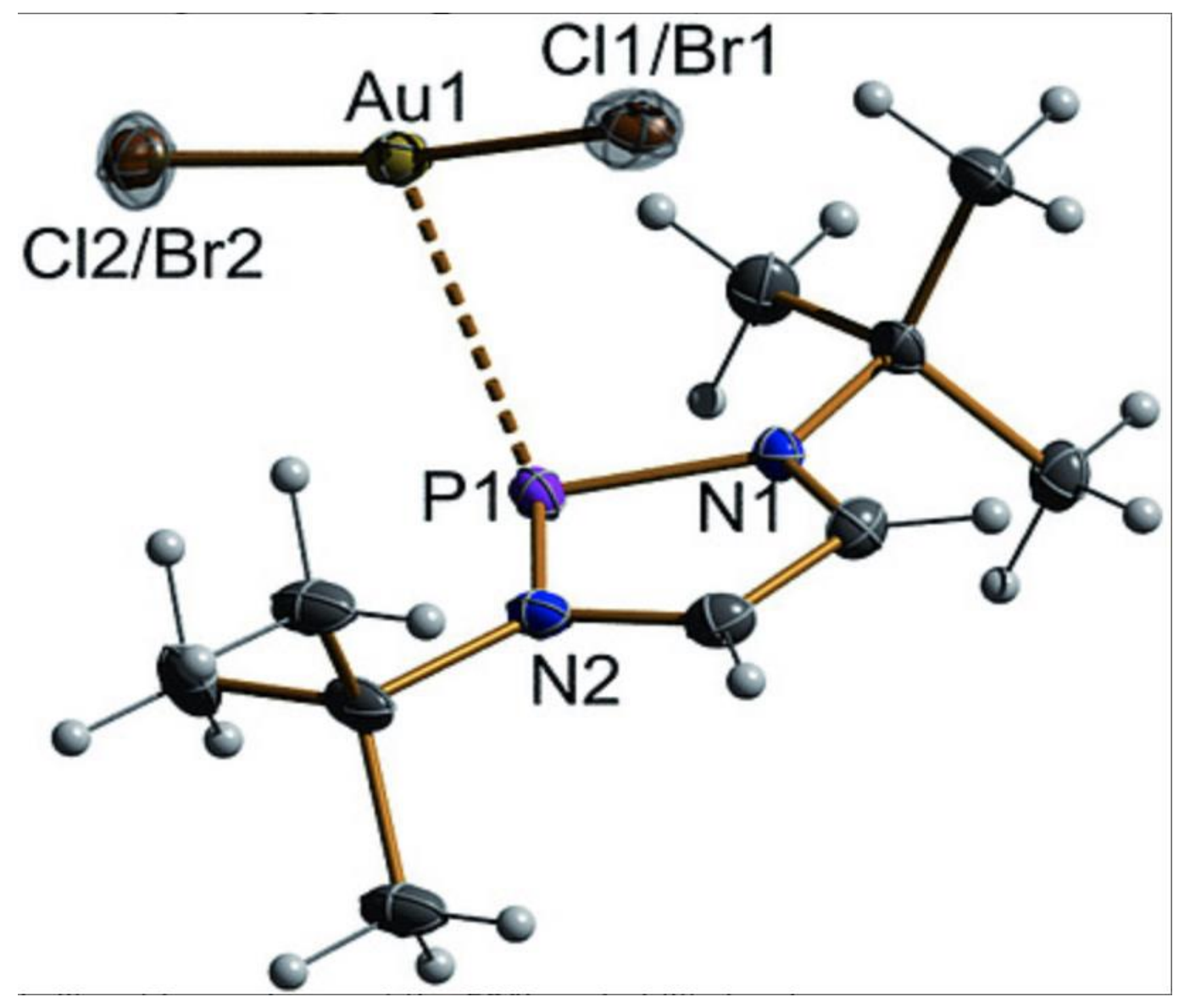
For example, Au-NHC complexes have been proven to be efficient catalysts in some addition reactions.[1]

In the Caputo group, we are interested in the differences in catalysis that might result when substituting the NHP ligand for the NHC at Au. We anticipate differences in reactivity due to the inverse electron demand of the NHCs vs. the NHPs.

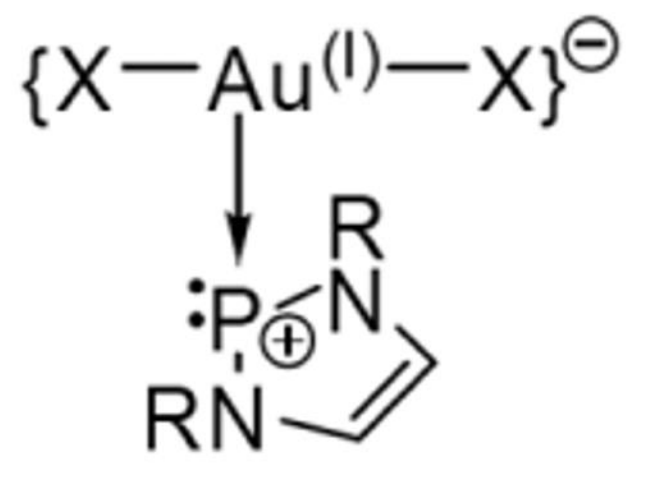
To that end, my goal is to synthesize a new NHP-Au complex where R = 2,4,6-trimethylphenyl (Mes) group and/or a 2,6-diisopropylphenyl (Dipp) group.

Literature Precedent

There is just one report by Gudat and co-workers that describes the synthesis of an NHP-Au complex, where R is ^{t}Bu.[3]



X-ray crystal structure of NHP-Au complex (R = ^{t}Bu) reported by Gudat and co-workers.[3] Thermal ellipsoids shown at 50% probability.

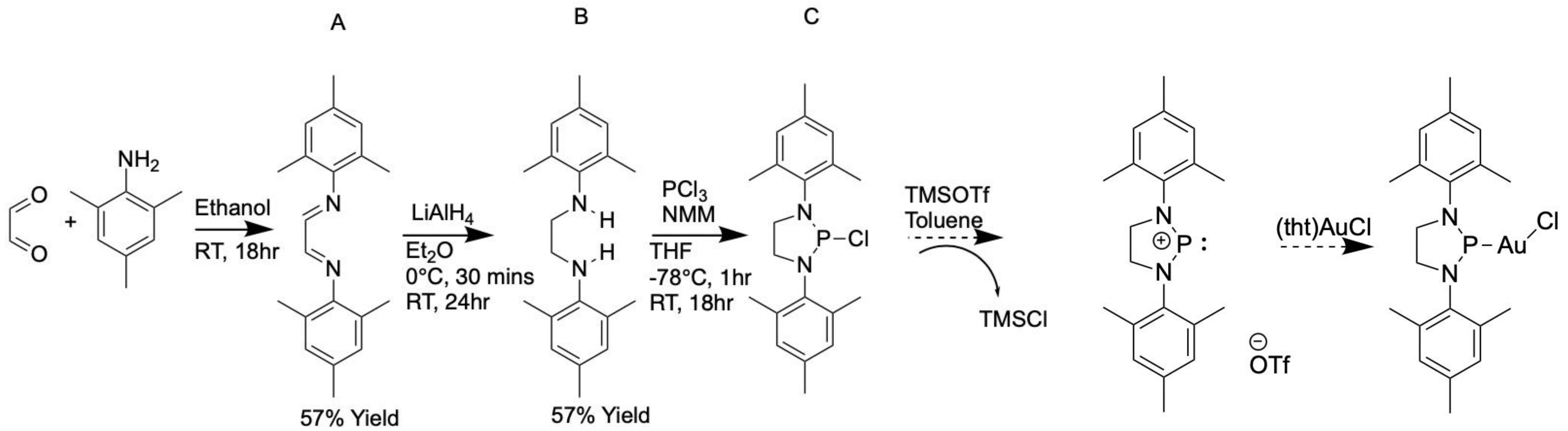


Note the N1-P1-Au1 bond angle is 98 °, indicating that the P lone pair is likely not involved in bonding to Au.

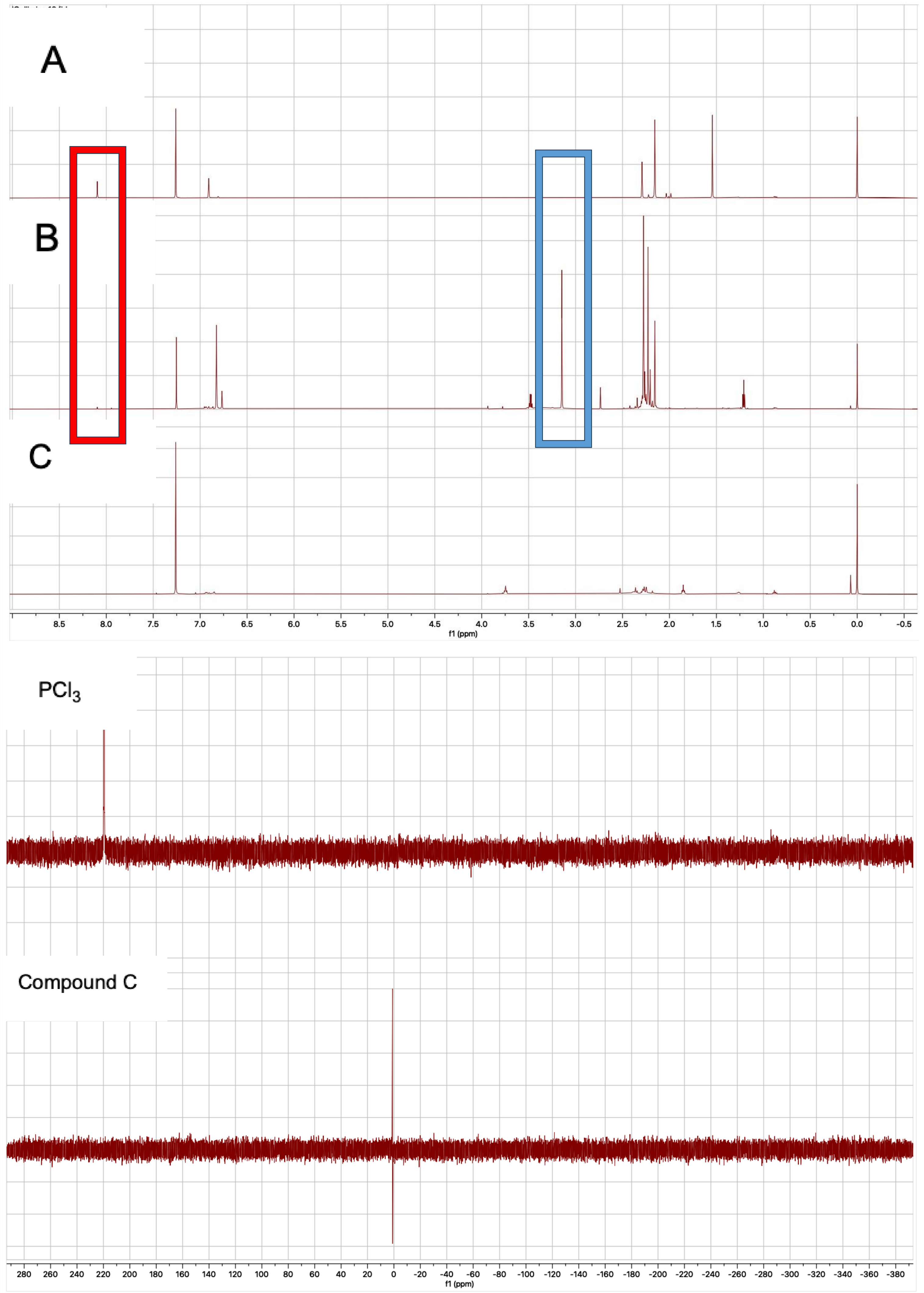
Instead, the Au d-electrons are back-bonding to the P empty p-orbital creating a pyramidal geometry at P.

Synthetic Scheme

Future Synthetic Steps



^{1}H and ^{31}P NMR Spectroscopic Characterization



Products A and B are characterized by the disappearance of the peak at 8.1 ppm, shown in the red box , which relates to the proton on the C=N bond, and the appearance of a peak around 3.2 ppm, shown in the blue box, which relates to the new N-H bond.

Product C is characterized by the same benzene proton peaks as the previous two, at around 6.9 ppm and the same methyl proton peaks at around 2.3 ppm. Additional peaks from 2-2.5 ppm are from NMM, and the peaks at 1.8 and 3.6 are from THF.

In the top ^{31}P NMR, the starting material phosphorus trichloride is shown and displays a peak around 225 ppm.

In the ^{31}P NMR on the bottom, a peak for the product is expected ~ 150-170 ppm. However, the only peak found on the spectrum is around 2 ppm. This is likely due to oxidation of the phosphorus creating a P=O bond.

The formation of the desired chlorophosphine intermediate will be repeated under more strictly inert conditions.

Conclusions

- Synthesis of N,N'-bis(2,4,6 trimethylphenyl)ethane-diamine successful and proven by ^{1}H NMR spectroscopy.
- Continue synthesis to create the targeted Au-NHP complex
- Confirm the complex structure using ^{1}H NMR and ^{31}P NMR spectroscopy and (hopefully) an X-ray crystal structure.
- Synthesize a second NHP using 2,6-diisopropylphenyl
- To use these AuNHP complexes in alkyne hydration catalysis
- Future work will include an investigation of NHP on Au nanoparticle surfaces or on Au electrodes for photo- or electrocatalytic applications.

Acknowledgements

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References

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