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Synthesis of Unsymmetrical Bidentate Ligands from Secondary Phosphine Oxides

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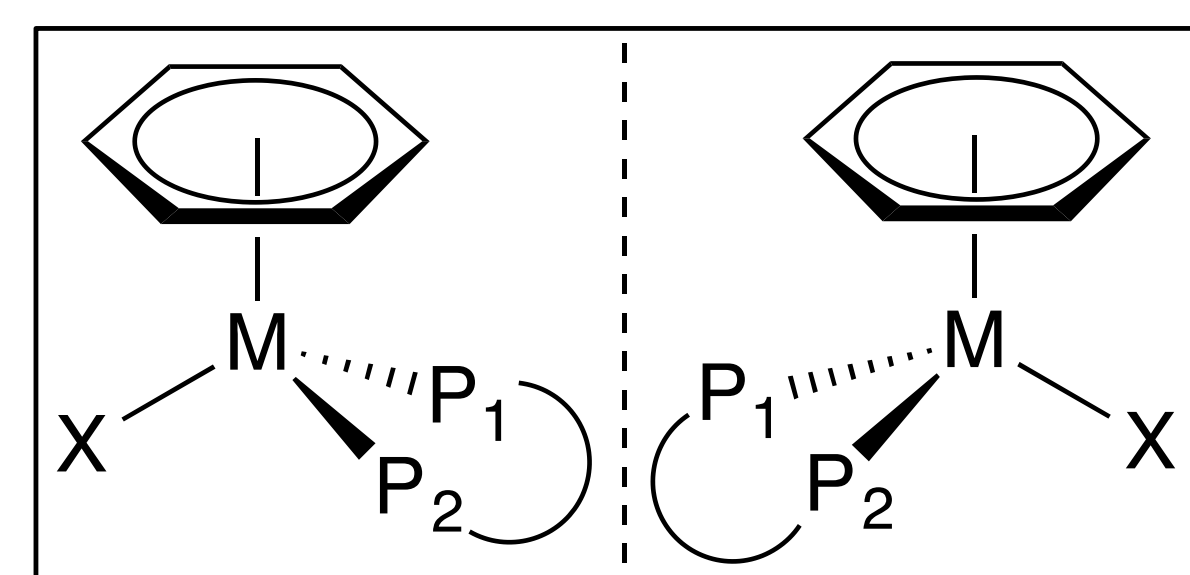
Synthesis of Unsymmetrical Bidentate Ligands from Secondary Phosphine Oxides

Malachy J. Brink, Ryan Anderson, and Bryan Nell

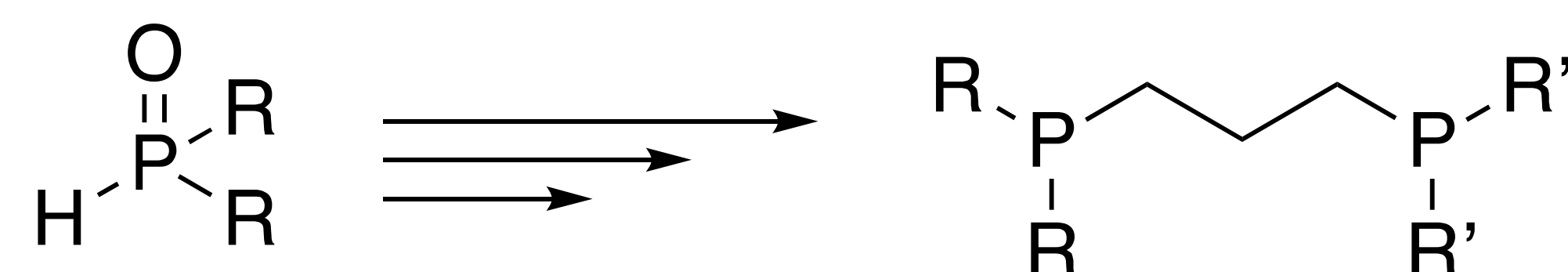
Division of Science and Mathematics, University of Minnesota Morris

Introduction

Stereochemistry is a key component in the field of asymmetric catalysis. The properties of a molecule can be drastically changed with the change of one stereocenter. Typically, chirality is imparted to a metal by the ligand. "Chiral-at-metal" compounds are unique because the metal complex is chiral, but the ligands are not.

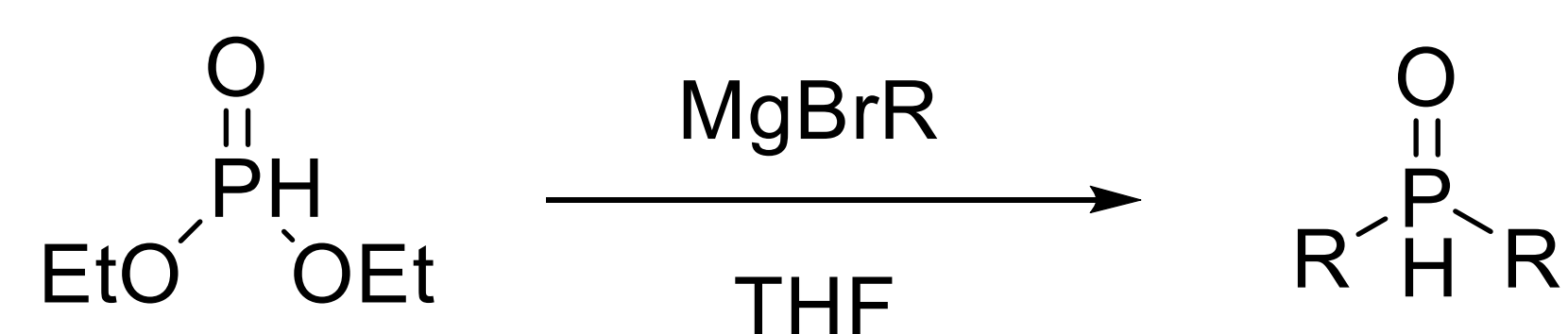


Phosphine ligands are notoriously difficult to work with (pyrophoric, toxic, prone to oxidation). The goal of this research was to prepare unsymmetrical bidentate ligands using secondary phosphine oxides, which are air-stable and easy to handle on the benchtop.



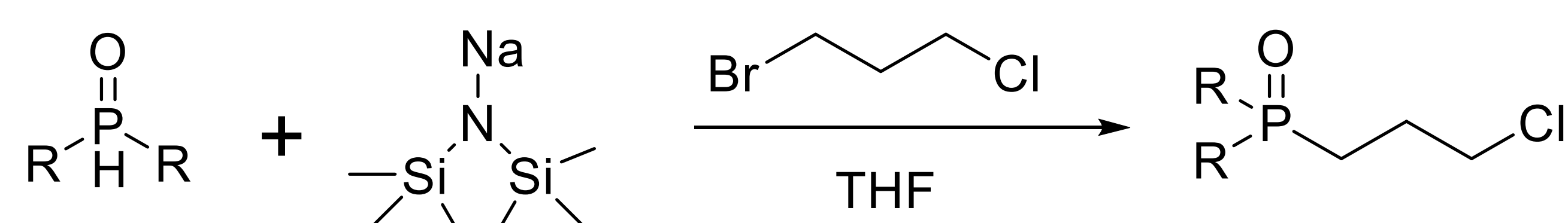
Experimental

- Initial reactions were run to prepare secondary phosphine oxides via Grignard reactions.



R= Me, Et, iPr, Cy, Ph

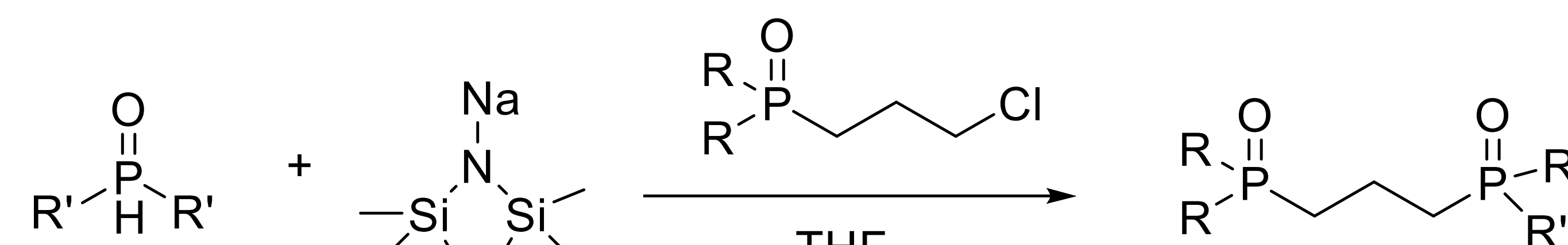
- Secondary phosphine oxides were deprotonated and reacted with 1-bromo-3-chloropropane to yield a tertiary phosphine oxide that is capable of another substitution.



R= Me, Et, iPr, Cy, Ph

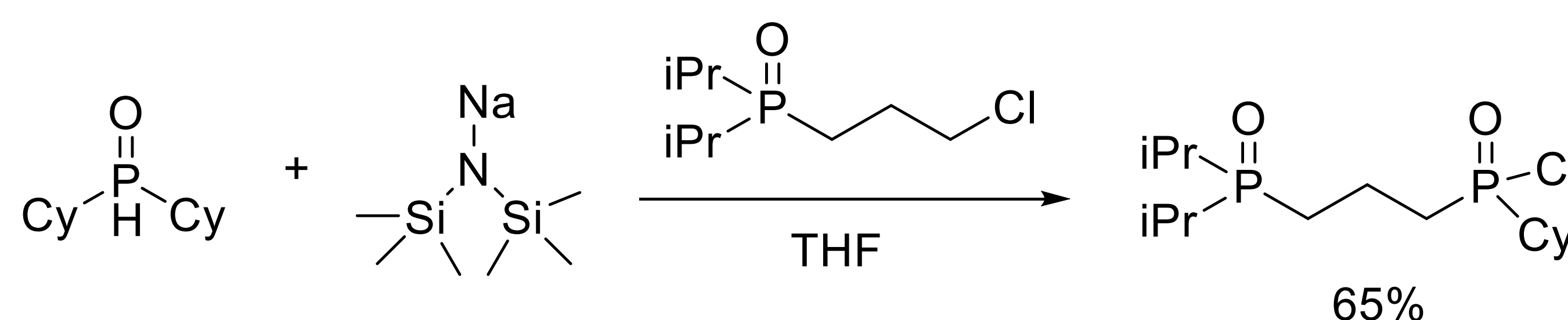
Experimental cont.

- Substitution with another secondary phosphine oxide gives an unsymmetrical bisphosphine oxide

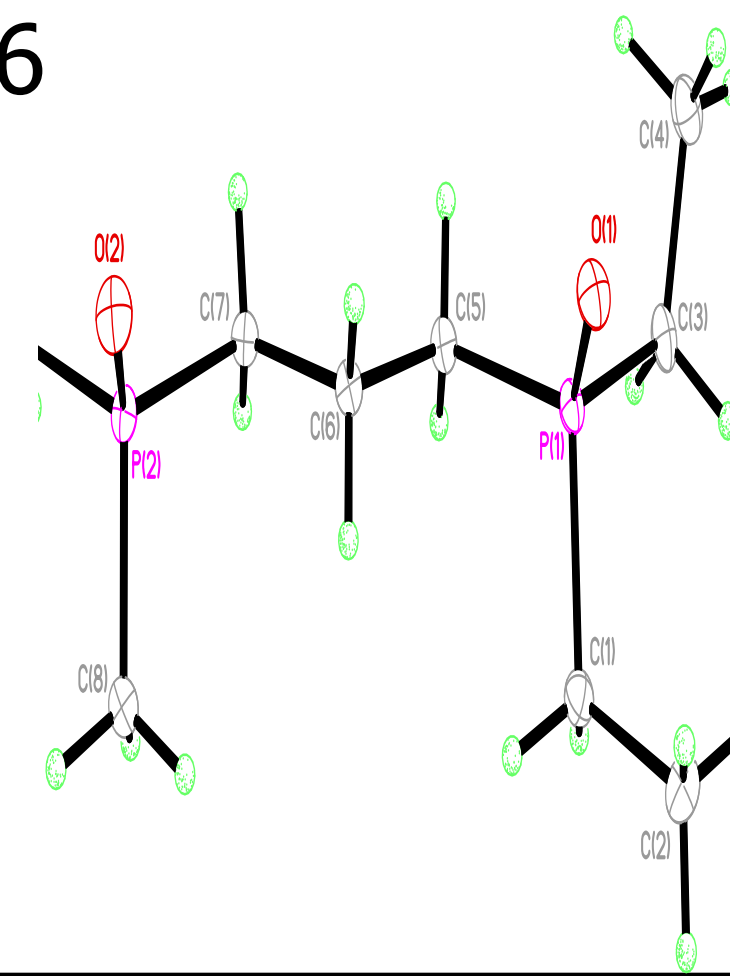


R= Me, Et, iPr, Cy, Ph
R'= Me, Et, iPr, Cy, Ph

- One of the ligands synthesized was as follows:

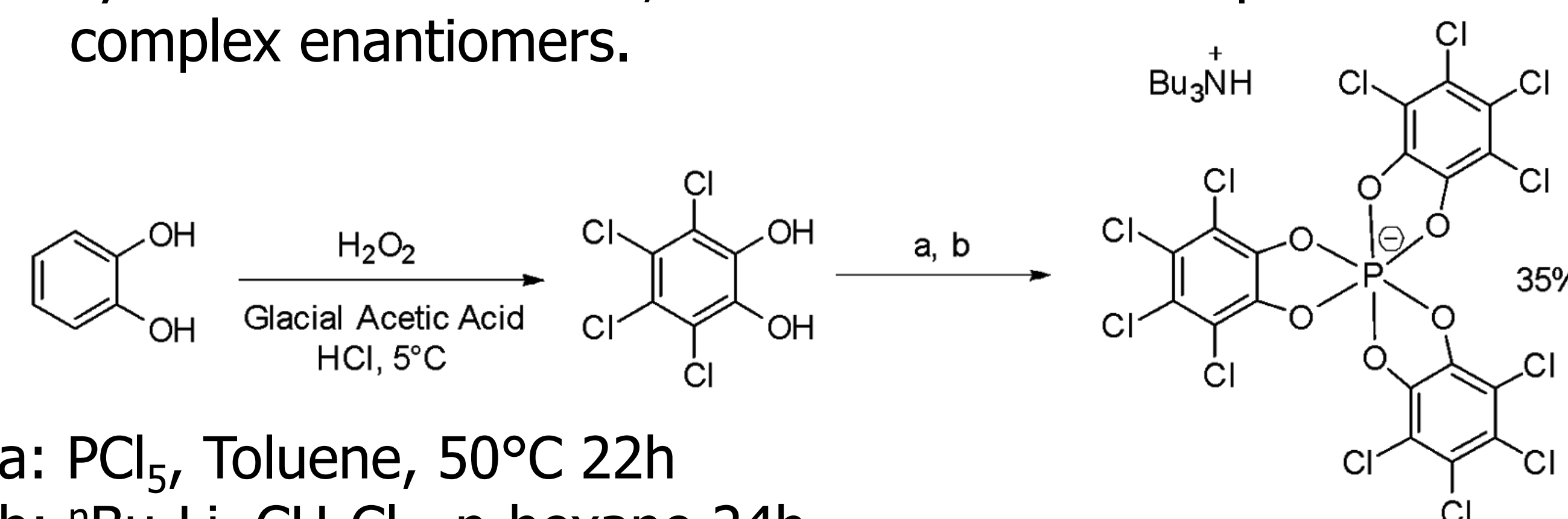


- ¹³C NMR (CDCl₃) δ 36.43 (d), 26.67 (dd), 26.29 (s), 25.99 (s), 25.66 (s), 25.28 (s), 16.19 (d), 15.99 (d), 15.82 (s). ³¹P NMR (CDCl₃) δ 56.34, 50.96



TRISPHAT

- The synthesis of chiral metal complexes results in a mixture of enantiomers. This research project also replicated the synthesis of TRISPHAT, a molecule used to separate metal complex enantiomers.



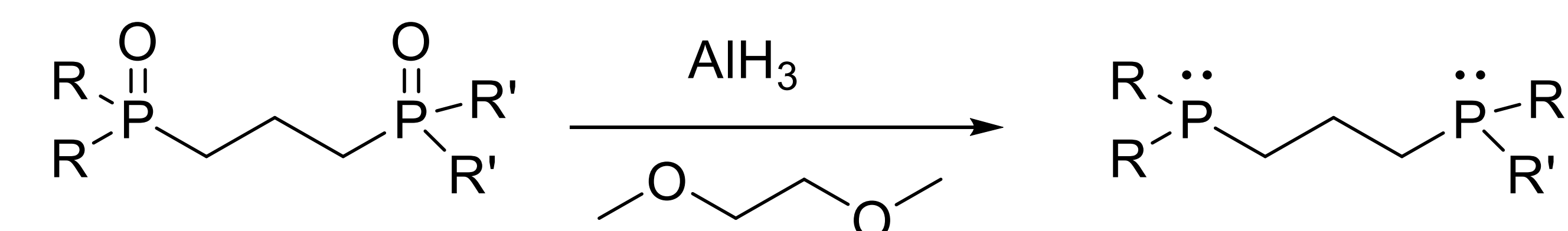
a: PCl₅, Toluene, 50°C 22h

b: ⁿBu₃Li, CH₂Cl₂, n-hexane 24h

¹³C NMR (CDCl₃) δ 141.0 (d), 123.76 (s), 54.09 (s), 25.66 (s), 19.91 (s), 13.53 (s). ³¹P NMR (CDCl₃) δ -80.91.

Conclusions and Future Research

- Secondary phosphine oxides are an ideal starting material for the synthesis of unsymmetrical phosphine oxides as they are easy to work with and air-stable.
- We have prepared a number of unsymmetrical bisphosphine oxides using this methodology in good yields and purity.
- After reduction with AlH₃, the resulting bisphosphines are good ligands for metal complexes. We are interested in using these compounds to create "chiral-at-metal" complexes capable of asymmetric catalysis



- With the synthesized Λ-TRISPHAT enantiomer, mixtures of metal complex enantiomers can be separated. Upon separation, the "chiral-at-metal" can act as catalysts for a variety of asymmetric processes.

Acknowledgements

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