

Synthesis of a novel ligand and inquiry into its capacity to support heterobimetallic bonding of transition metals

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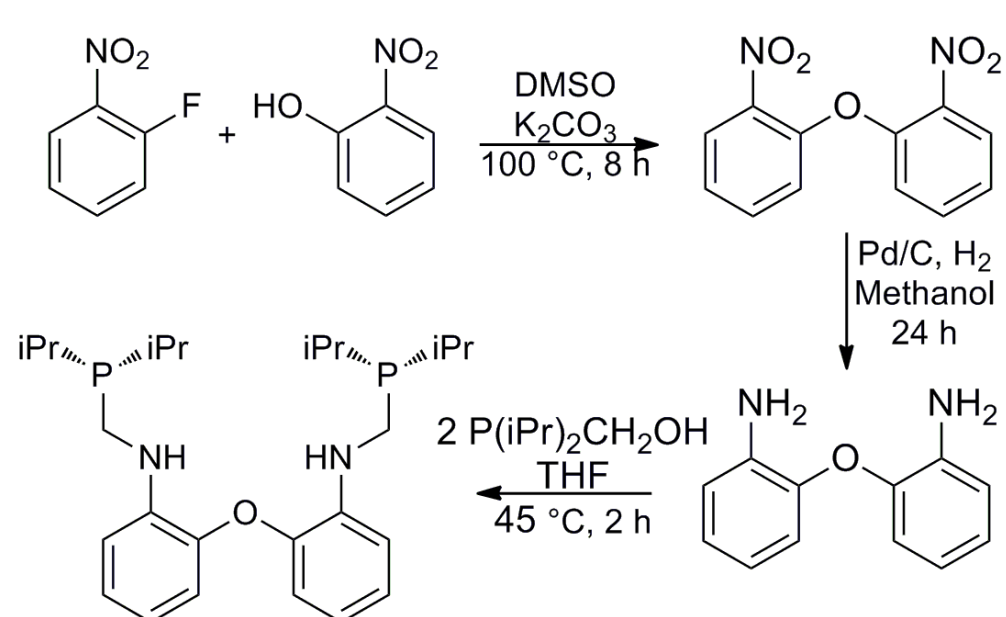
Introduction

Inorganic chemistry and organometallic chemistry are growing fields, with increased interest being placed on molecules containing two bonded metals. Some of these bimetallic complexes have been shown to exhibit interesting reactivity with substrate molecules, making them particularly useful in the study of small molecule reduction. Many chemists are interested in mimicking metal-containing enzymes that exhibit this type of reactivity help scientists and engineers better understand these molecules and emulate them in economical and environmentally conscious ways.

Goals

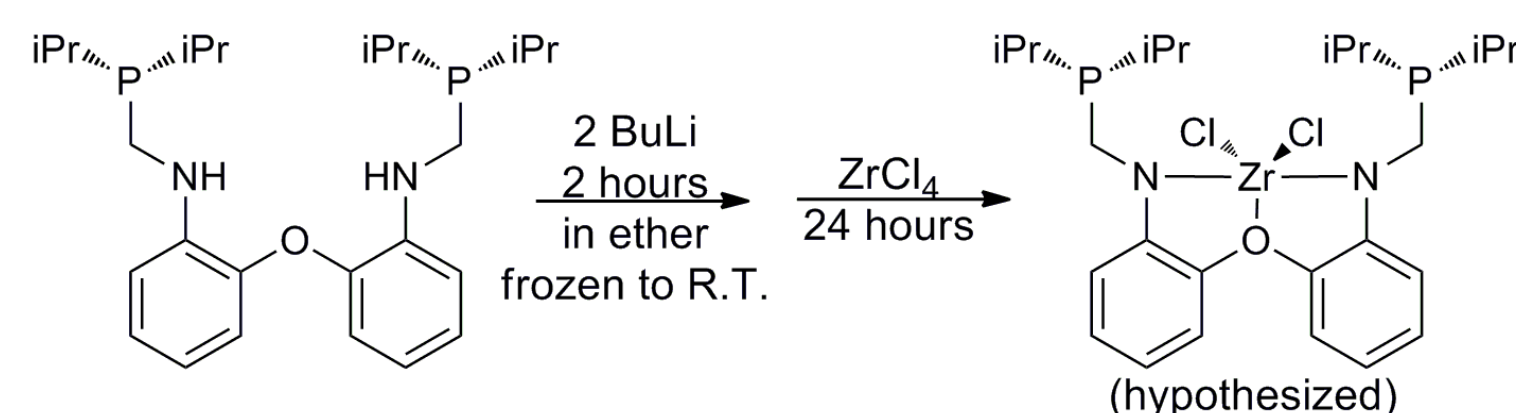
- To synthesize a novel ligand that is capable of supporting up to two metal centers
- To incorporate one to two metals into the ligand.

The Ligand

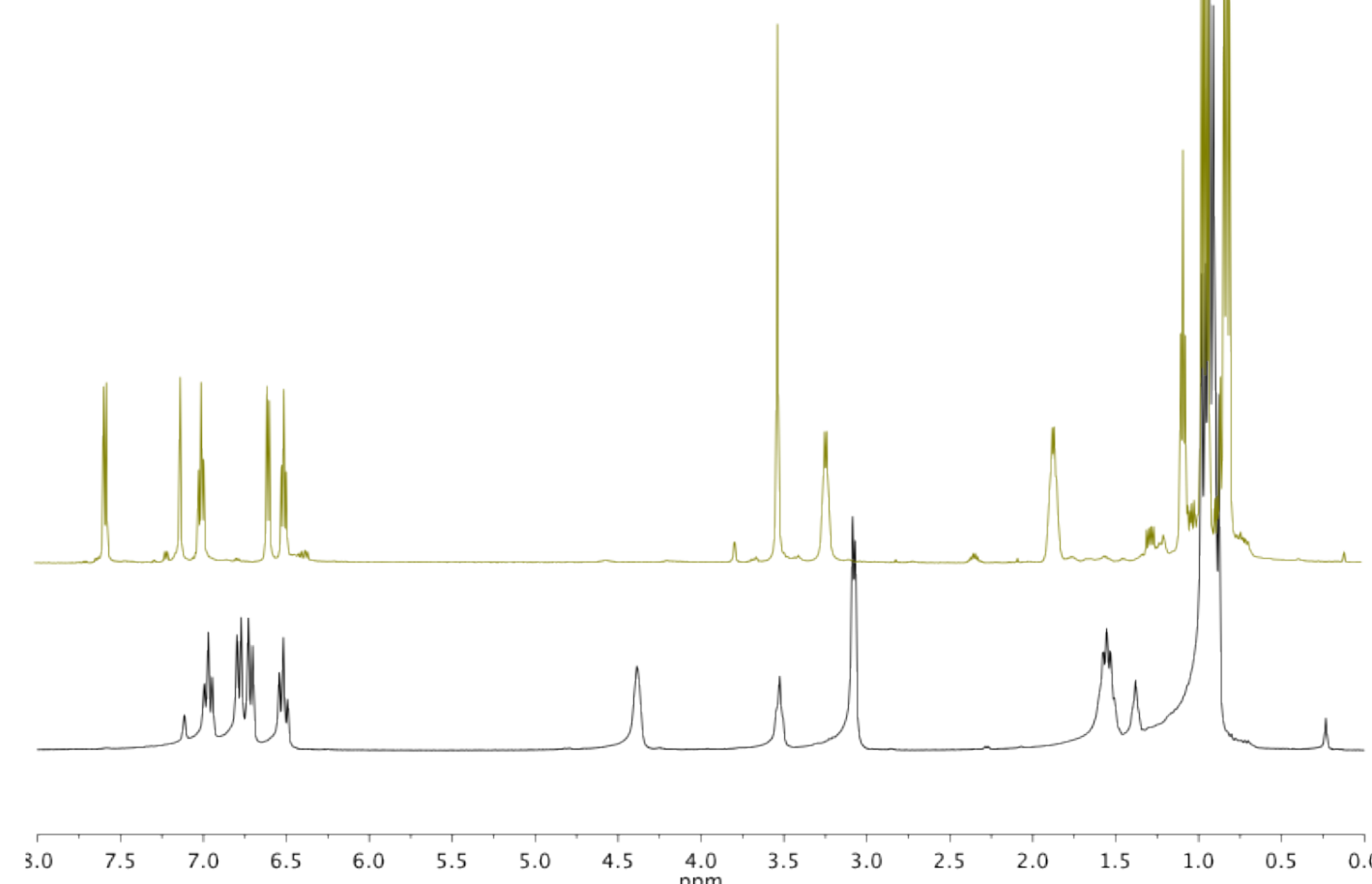


- Ligand is synthesized in four relatively simple steps with an overall yield of 40%
- Two similar ligands were synthesized prior to PNONPiPr. In both, an NH group replaced the oxygen atom in the ligand's base. Both phenyl and isopropyl phosphine derivatives were synthesized. These ligands, PNNNP^{Ph} and PNNNP^{iPr}, decomposed and showed poor reactivity, so the new ligand, PNONPiPr, was synthesized.
- When deprotonated, PNONPiPr has a -2 charge, which encourages binding of an early transition metal in the nitrogen/oxygen pocket.
- The phosphines provide a bonding site for the second metal.

Zirconium Monometallic

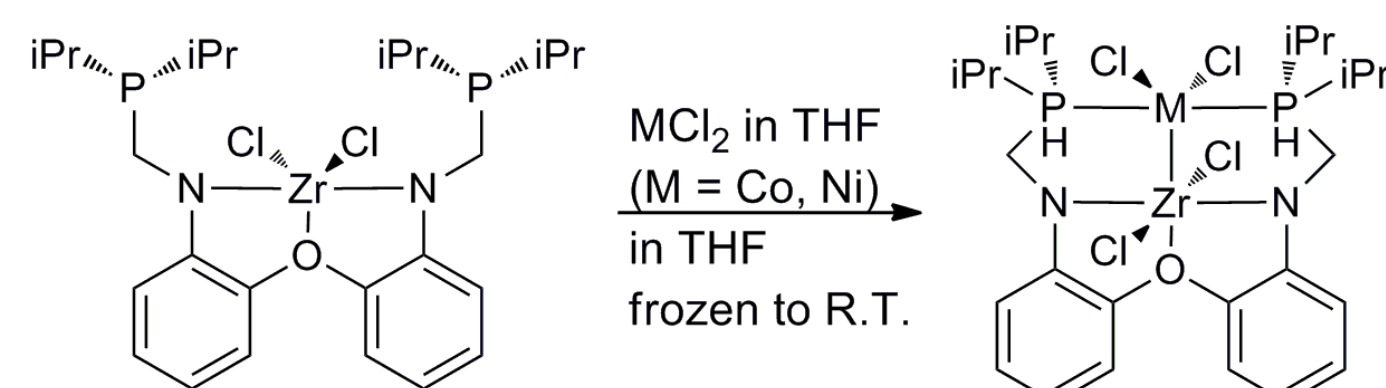


- The reaction, performed in ether, turned bright yellow upon addition of ZrCl₄.
- Clear differences are observed by ¹H NMR and ³¹P NMR, including new shifts of isopropyl and aryl protons and no observed amine protons in the metaloligand.
- Other monometallic syntheses beginning with precursors such as TiCl₄, Ti(NMe₂)₄, PdCl₂, AlCl₃, CoCl₂, and ZnCl₂ were also attempted but did not show promising results.

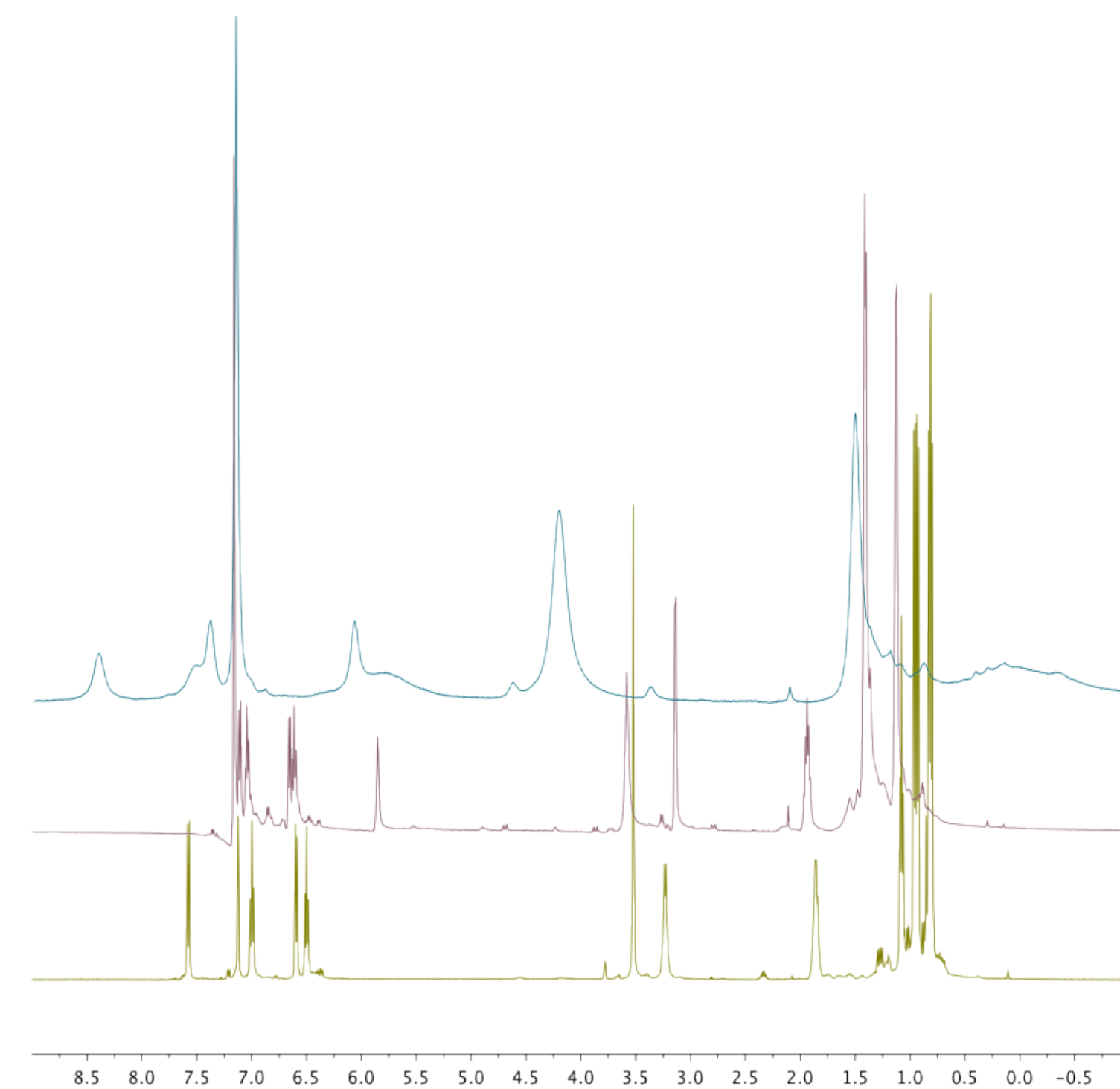


Above: ¹H NMR spectra of PNONPiPr (bottom, black) and PNONPiPr•ZrCl₂ (top, yellow). Phosphorus chemical shifts occurred at 2.88 ppm for PNONPiPr and 8.41 ppm for PNONPiPr•ZrCl₂

Bimetallics



- Metallations of PNONPiPr•ZrCl₂ with NiCl₂ and CoCl₂ resulted in drastic color changes (yellow to dark pink and dark teal, respectively) showed promising initial results by ¹H NMR and ³¹P NMR, though the reaction with CoCl₂ appears to decompose in solution after 3 to 4 hours.



Above: ¹H NMR spectra of PNONPiPr•ZrCl₂•CoCl₂ (top, teal), PNONPiPr•ZrCl₂•NiCl₂ (middle, pink), and PNONPiPr•ZrCl₂ (bottom, yellow).

Results and Future Work

- Initial characterization suggest the Zirconium monometallic was synthesized in high purity. Additionally, Co-Zr and Ni-Zr bimetallics seem promising.
- Future work will involve using x-ray crystallography to verify the structure of these compounds. If crystals are promising, UV-Vis, IR, MS, and CV may be used to characterize these compounds. Additionally, reactivity with small molecules may be examined.

Acknowledgments

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