Synthesis of First-Row Transition Metal Catalysts for Alkene Hydroamination

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Objective

- To develop an efficient synthesis for a catalyst to be used in an hydroamination reaction utilizing imino-phosphine ligands and first-row transition metals.

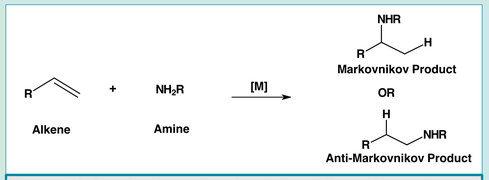

Figure. 1 Hydroamination reaction of a substituted alkene with an amine utilizing a metal complex catalyst.

Background

- Nitrogen containing compounds, amines, represent a vital component to countless industries, with applications including simple dyes to cleaning products.[1]
- Currently, there is a rising need for inexpensive and efficient synthetic methods for amines.
- The hydroamination reaction is a very attractive route due to its simplicity and proposed 100 % atom efficiency.[1,2,3]
- Efforts have been focused towards developing catalysts that increase hydroamination efficiency.
- Many of these catalysts utilize precious metals that are heavy, non-abundant, expensive and hazardous to health.[4]
- This research focuses on developing economically and environmentally conscious catalysts with first-row transition metals.

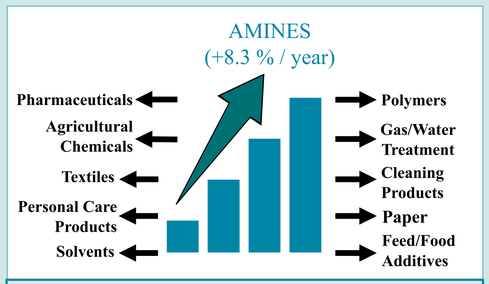

Figure. 2 Applications of amines. Reproduced from Ref. 1.

References

1. Streiff, S.; Jérôme, F. *Chem. Soc. Rev.,* **2021**, *50,* 1512-1521.
2. Pohlki, F.; Doye, S. *Chem. Soc. Rev.,* **2003**, *32,* 104-114.
3. Müller, T.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008,** *108,* 3795-3892.
4. Ludwig, J. R.; Schindler, C. S. *Chem.* **2017**, *2,* 313-316.
5. Motswainyana, W. M., Onani, M. O., Madiehe, A. M., Saibu, M., Thovhogi, N., Lalancette, R. A. *J. Inorg. Biochem.* **2013,** *129*, 112-118.

Experimental and Methodology

Method

Synthesis of Imino-Phosphine Ligands

- The novel imino-phosphine ligands were synthesized through a Schiff base condensation of 2-diphenylphosphino benzaldehyde, 2-DPPB, and corresponding anilines, including 2,4,6-triphenylanilne (Ligand 1) and 4-tritylaniline (Ligand 2), as shown in Tables. 1 and 2.

Coordination of Ligand 2

- The synthesized Ligand 2 was then coordinated to zinc chloride and cobalt (II) chloride by refluxing in diethyl ether.

Characterization

All NMR and IR characterizations were obtained on a Bruker Avance 500 MHz NMR spectrometer and Perkin Elmer FT-IR spectrometer respectively.

- The imino-phosphine ligands were both characterized through ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, as well as FT-IR spectroscopy.
- Ligand 2 coordinated to zinc chloride was characterized through ^{1}H NMR spectroscopy.

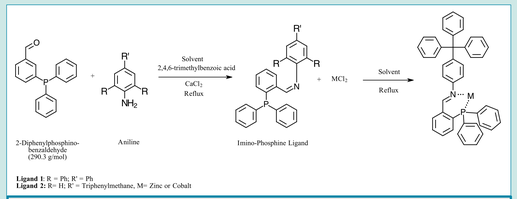

Figure. 3 Reaction mechanism for synthesis of Ligand 1 and Ligand 2 as well as the mechanism for coordination of $CoCl_2$ and $ZnCl_2$ to Ligand 2.

Table. 1 Reaction conditions for synthesis of imino-phosphine ligands.

Reaction	2-DPPB (g)	2,4,6-TPA (g)	2,4,6-TMBA (g)	$CaCl_2$ (g)	Reflux Time (h)	Yield (g)	Percent Yield
Ligand 1	0.06572	0.07768	0.1208	0.0738	2.5	0.09638	70.1 %
Ligand 2	0.3408	0.3762	0.1991	0.3746	3.5	0.64549	97.0 %

Table. 2 Reaction conditions for coordination of zinc to Ligand 2.

Metal	Metal (g)	Ligand 2 (g)	Solvent	Reflux Time (h)	Yield (g)	Percent Yield
Zinc Chloride	0.10	0.10	Ethyl Ether	1.5	0.06493	58.4 %
Cobalt (II) Chloride	0.10	0.10	Ethyl Ether	1.5	N/A	N/A

Results and Discussion

^{1}H NMR Characterization of Ligands 1 and 2

- ^{1}H NMR characterizations of both imino-phosphine ligands proved to be successful as shown in Figures. 6 and 7.
  - The imine protons are shown as doublets at 8.93 ppm and 9.16 ppm for Ligand 1 and Ligand 2 respectively. The doublet suggests that the imine proton is coupling to the phosphorus lone pair.[5]
  - By decoupling ^{31}P in the ^{1}H NMR, we were able to prove that the imine proton is coupled to the phosphorus atom as the characteristic peaks reverted to singlets, as shown in the top left of Figures. 6 and 7.

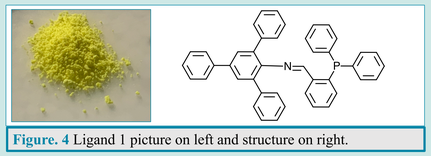

Figure. 4 Ligand 1 picture on left and structure on right.

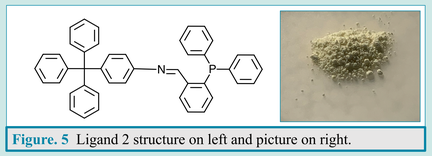

Figure. 5 Ligand 2 structure on left and picture on right.

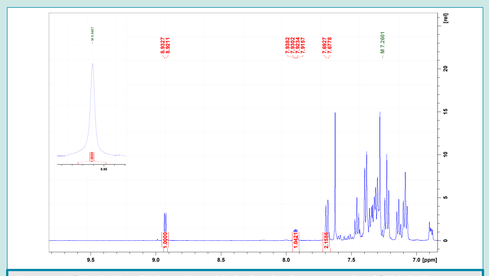

Figure. 6 ^{1}H NMR of Ligand 1 with imine hydrogen peak of ^{1}H NMR spectra with ^{31}P decoupled (top left).

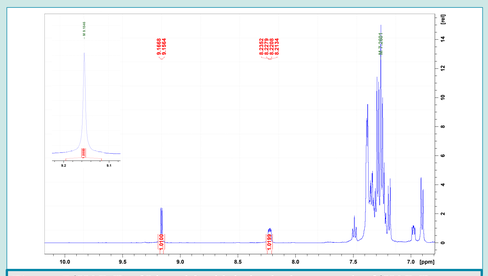

Figure. 7 ^{1}H NMR of Ligand 2 with imine hydrogen peak of ^{1}H NMR spectra with ^{31}P decoupled (top left).

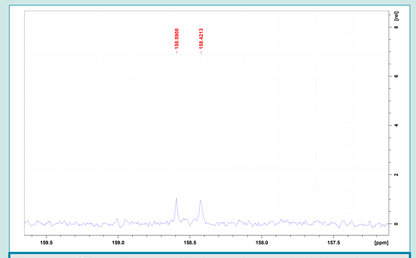

Figure. 8 ^{13}C NMR spectral imine carbon peak of Ligand 1.

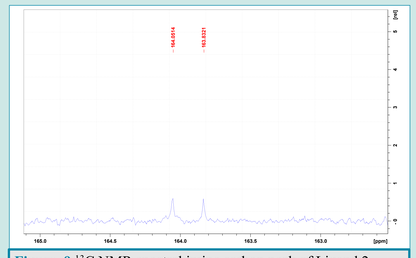

Figure. 9 ^{13}C NMR spectral imine carbon peak of Ligand 2.

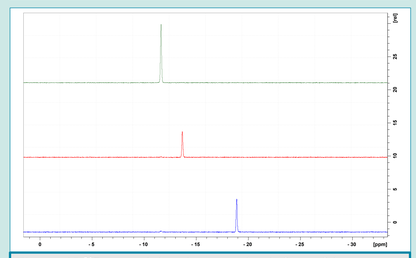

Figure. 10 ^{31}P spectral data depicting the shifting of the phosphorus peak between 2-DPPB (top), Ligand 2 (middle), and Ligand 1 (bottom).

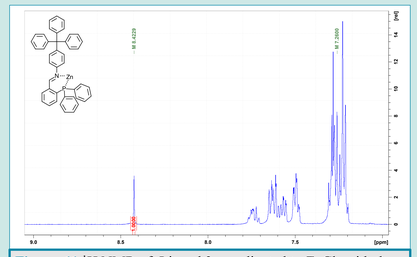

Figure. 11 ^{1}H NMR of Ligand 2 coordinated to $ZnCl_2$ with the structure demonstrated in the top left.

^{13}C Characterizations of Ligands 1 and 2

- The ^{13}C spectra of each ligand indicate a doublet for the imine carbon, as shown in Figures. 8 and 9. Similar to the doublet demonstrated by the imine protons in the ^{1}H NMR, the doublets for the imine carbon in the ^{13}C spectra can be attributed to a through space coupling to the phosphorus lone pair.

^{31}P Characterizations

- As shown in Figure. 10, shifting patterns are demonstrated between 2-DPPB (starting material) and the newly synthesized Ligands 1 and 2.
  - 2-DPPB, the starting material, was shown to be the furthest downfield due to the electronegative oxygen present.
  - Interestingly, the phosphorus peak of Ligand 2 is further downfield than the phosphorus peak for Ligand 1.

FT-IR Characterizations of Ligands 1 and 2

- Absorption frequencies at 1633.78 cm^{-1} and 1615.24 cm^{-1} for Ligand 1 and Ligand 2 respectively are characteristic of $\nu_{C=N}$ stretching vibration bands, confirming the synthesis of the imino-phosphine ligands.

^{1}H NMR of Coordinated Ligand 2

- Coordination of the Ligand 2 proved to be successful utilizing $ZnCl_2$, as shown in Figure. 11.
  - The singlet of the imine proton at 8.42 ppm demonstrate a strong coordination between the imine nitrogen and the phosphorus metal centre.
  - Compared to the uncoordinated ligand, the imine proton of the complexed ligand shifted up-field. This is seen to be characteristic of imine coordination and is a result of electron density from the newly introduced metal shifting towards the electronegative nitrogen.[5]

Conclusion

- This research successfully developed an efficient synthetic method of two novel imino-phosphine ligands with a 70.1 % yield using 2,4,6-triphenylaniline and 97.0 % yield using 4-tritylaniline.
- Structural characterizations via ^{1}H, ^{13}C, ^{31}P NMR and FT-IR spectroscopy of both imino-phosphine ligands elucidated coupling patterns and confirmed imine formation.
- The synthesized 4-tritylaniline successfully coordinated to zinc chloride as demonstrated by ^{1}H NMR data, however further structural elucidation via x-ray crystallography is needed to confirm coordination to cobalt (II) chloride.

Future Work

- Next steps should include coordinating other first-row transition metals to the imino-phosphine ligands, such as iron and nickel, as well as assess the catalyst's abilities in hydroamination reactions.