1,2-bis(diphenylphosphino)ethane (dppe) and Ni(dppe)Cl₂ synthesis via solvated electron reduction

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Abstract

This experiment demonstrated successful synthesis of the dppe ligand via solvated electron reduction of triphenylphosphine followed by treatment with 1,2-dichloroethane, as well as ligand substitution of $NiCl_2 \cdot 6 H_2O$ to yield $Ni(dppe)Cl_2$. The reaction had an overall yield of 117.74% for dppe and 47% for $Ni(dppe)Cl_2$. ^1H NMR, ^{31}P NMR, and IR spectra of dppe and $Ni(dppe)Cl_2$ were analyzed, and confirmed experimental success while noting the presence of excess solvent and residual impurity. Future studies should improve upon this synthesis by minimizing residual solvent, improving $Ni(dppe)Cl_2$ yield via temperature control, and using higher resolution NMR instruments to characterize dppe.

Introduction
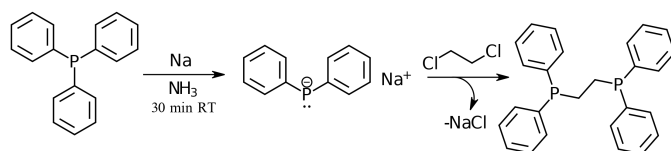
Scheme 1: Synthesis of dppe via reduction of triphenylphosphine followed by reaction with 1,2-dichloroethane.

Ammonia is a versatile inorganic solvent with the unique property of dissolving alkali metals to form solvated electrons, which act as extremely strong reducing agents in solution. In this experiment, this property was used to reduce a solution of triphenylphosphine to yield the bidentate ligand 1,2-bis(diphenylphosphino)ethane (dppe) upon reaction with 1,2-dichloroethane. The dppe was used to perform ligand substitution on $NiCl_2 \cdot 6 H_2O$, generating its corresponding complex $Ni(dppe)Cl_2$. This experiment demonstrates the efficacy of cheap, readily-available reagents to synthesize useful coordinating ligands for use in laboratory and industry.
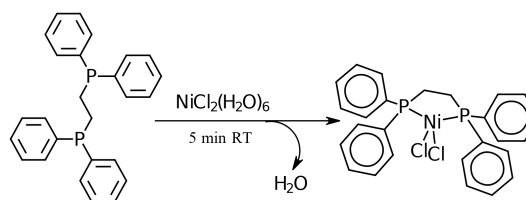
Scheme 2: Synthesis of $Ni(dppe)Cl_2$ via direct ligand substitution of $NiCl_2 \cdot 6 H_2O$.

Results and Discussion

The experiment resulted in a 117.74% yield of dppe, and a 47% yield of $Ni(dppe)Cl_2$. Consequentially, the dppe was either not fully dry

prior to NMR and IR analysis, or it contained some residual impurity. The yield of $Ni(dppe)Cl_2$ is interesting as well, as it implies that the ligand substitution reaction (Scheme 2) was not driven to completion. This could be a result of either poor kinetics arising from reaction conditions (room temperature, short reaction time), or thermodynamic effects driving the reaction towards dissociation due to steric effects of the dppe ligand, though this is unlikely as polydentate ligands are known to be highly stable.[1]

To further investigate these findings, the 60 MHz ^{1}H and 400 MHz ^{31}P NMR spectra taken in $CDCl_3$ were analyzed. The ^{1}H NMR spectrum of dppe was rather poor; diethyl ether was a prominent impurity, and shifts corresponding to the aromatic hydrogens were not discernible in the ^{1}H NMR spectra. These are due both to the poor resolution of the 60 MHz instrument and the overlap with the solvent $CDCl_3$ peak. This statement is supported by the integration of 20 aromatic protons underneath the broad peak $\delta = 7.27$ ppm, exactly corresponding to the 20 aromatic protons of the 26 in dppe. This finding has been replicated in other ^{1}H NMR spectra of dppe.[2]

This hypothesis is further supported by the ^{1}H NMR spectrum of $Ni(dppe)Cl_2$, which was able to distinguish the same aromatic protons from the $CDCl_3$ shift. This is because the presence of the Ni^{2+} metal center withdraws electron density from the lone pairs of phosphorus and the aromatic protons, causing them to appear further downfield and distinguishing the protons meta to phosphorus from those that are ortho or para to phosphorus.

The ^{31}P NMR spectra were not particularly revealing, as there exists only one chemically distinct phosphorus atom in both dppe and $Ni(dppe)Cl_2$. However, there was an unknown impurity at $\delta = $ -105.91 ppm and $\delta = $ -221.00 ppm observed in both ^{31}P NMR spectra. This finding was not replicated elsewhere, suggesting that its corresponding impurities are unique to this synthetic method or the materials used in this experiment.

Aside from the aforementioned impurities and the ^{1}H NMR multiplicities (indistinguishable
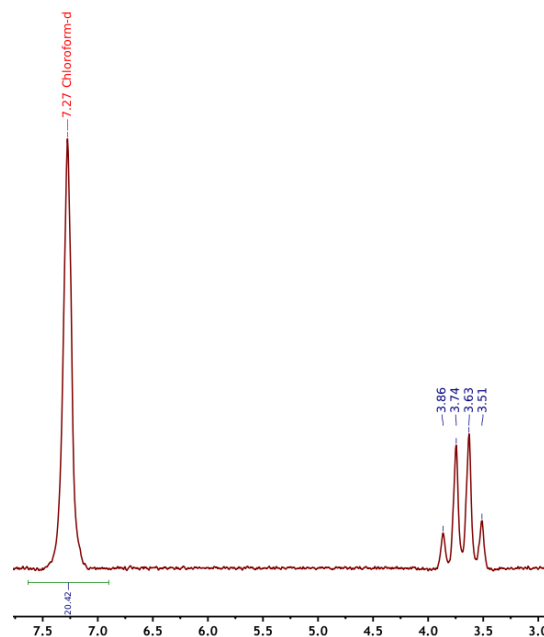

Figure 1: ^{1}H NMR of dppe, magnified to highlight the aromatic shifts at $\delta = 7.27$ ppm (20 H). Note the overlap with the existing $CDCl_3$ peak and the diethyl ether signal ($\delta = 3.68$ ppm, q).
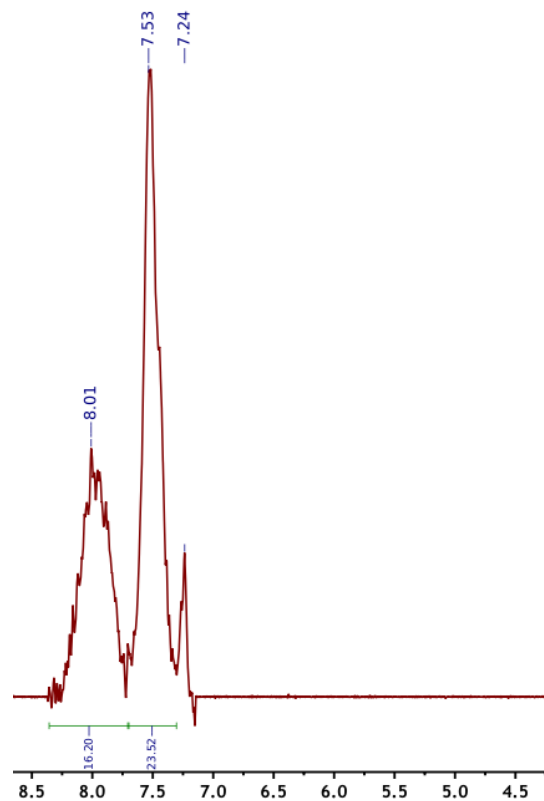

Figure 2: ^{1}H NMR of dppe, magnified to highlight the aromatic shifts at $\delta = 8.01$ ppm (16 H) and $\delta = 7.53$ (24 H). Note the distinguished $CDCl_3$ peak ($\delta = 7.24$ ppm) upon formation of the nickel complex.

due to the poor resolution), the chemical shifts of both the ^{1}H and ^{31}P spectra are in good agreement with existing studies done on dppe and Ni(dppe)Cl$_2$.[2,3]

The IR spectrum of dppe was not noteworthy, and indicated exclusively a C-H stretch and an O-H impurity. Interestingly, the IR spectrum of Ni(dppe)Cl$_2$ was completely absent in the 3000-4000 cm^{-1} region. This is in fact largely consistent with existing IR studies on Ni(dppe)Cl$_2$,[4] which indicate exceedingly weak C-H stretches in Ni(dppe)Cl$_2$.

In conclusion, this experiment demonstrated the successful synthesis of the dppe ligand via solvated electron reduction of triphenylphosphine followed by treatment with 1,2-dichloroethane, as well as ligand substitution to yield Ni(dppe)Cl$_2$. As indicated by the ^{1}H NMR, ^{31}P NMR, and IR analysis, future studies should improve upon this synthesis by minimizing residual solvent, improving Ni(dppe)Cl$_2$ yield via temperature control, and using higher resolution NMR instruments to characterize dppe.

Experimental Procedures

dppe synthesis:[5] To a round bottom flask was charged 200 mL of NH$_3$, a glass-coated stir bar, and a dry ice condenser. Na (2.379 g, 0.1035 mol, 4 equiv.) was added slowly over 3 minutes. A dark blue solution was allowed to form over 10 minutes, and then triphenylphosphine (13.55 g, 0.05166 mol, 2 equiv.) was added in 1 g portions. This solution reacted for 30 minutes, after which NH$_4$Br (5.068 g, 0.05174 mol, 2 equiv.) was added. 1,2-dichloroethane (2.555 g, 0.02582 mol, 1 equiv.) was poured in and reacted for 10 minutes. The flask was left open to air for 1 week.

The dried dppe was washed with DI water and rotary evaporated following dilution with ethanol. The purified dppe crystals then precipitated, and were filtered out of solution and washed with ethanol.

Ni(dppe)Cl$_2$ synthesis:[5] NiCl$_2\cdot$6 H$_2$O (0.320 g, 1.34 mol, 1 equiv.) was dissolved in ethanol and mixed with dppe (0.54 g, 1.34 mol, 1 equiv.). This was allowed to react for 5 minutes, forming a tomato-red solution. Ni(dppe)Cl$_2$ was filtered out and washed with diethyl ether. ^{1}H, ^{31}P NMR and IR spectra were taken of dppe and Ni(dppe)Cl$_2$, and are available for viewing in the Supporting Information.

References

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