

# 1,2-bis(diphenylphosphino)ethane (dppe) and Ni(dppe)Cl<sub>2</sub> synthesis via solvated electron reduction

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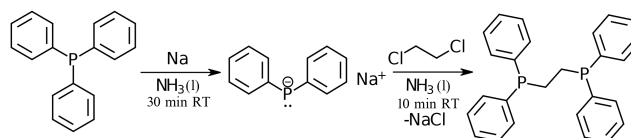
## Abstract

This experiment demonstrated successful synthesis of the dppe ligand via solvated electron reduction of triphenylphosphine followed by treatment with 1,2-dichloroethane. Subsequent ligand substitution of NiCl<sub>2</sub> · 6 H<sub>2</sub>O yielded Ni(dppe)Cl<sub>2</sub>. The reaction had an overall yield of 117.74% for dppe and 47% for Ni(dppe)Cl<sub>2</sub>. <sup>1</sup>H NMR, <sup>31</sup>P NMR, and IR spectra of dppe and Ni(dppe)Cl<sub>2</sub> 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<sub>2</sub> yield via temperature control, and using higher resolution NMR instruments to characterize dppe.

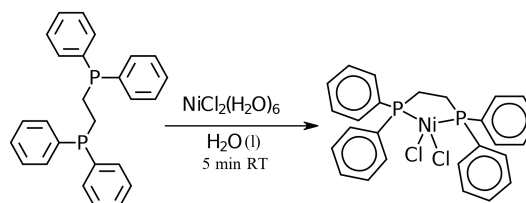
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Economical synthesis of ligands and metal complexes using readily available reagents are of vital importance in both laboratory and industry. Polymer chemistry relies almost entirely on catalysts formed from these reactions. The Ziegler-Natta metallocene catalysts (e.g. Cp<sub>2</sub>ZrCl<sub>2</sub>), which are still used today to generate polyethylene, are one famous example. Their efficacy depends on the metallocene ligands, which occupy multiple coordination sites while being too sterically hindered to fully chelate the metal ion. This property prevents excessive termination and other undesirable reactions during polymerization.<sup>1</sup>

A bulky, polydentate ligand such as dppe shares this property, making dppe complexes useful polymerization catalysts. This catalytic ability is exhibited in Ni(dppe)Cl<sub>2</sub>, which is already known to promote chain growth and cross-coupling of aromatic molecules.<sup>2,3</sup>



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



Scheme 2: Synthesis of Ni(dppe)Cl<sub>2</sub> via direct ligand substitution of NiCl<sub>2</sub> · 6 H<sub>2</sub>O.

This experiment aimed to achieve economical synthesis of both the dppe ligand and

Ni(dppe)Cl<sub>2</sub> ligand for use in polymer chemistry. The synthetic route thus needed to maximize usage of readily available reagents for synthesis. Thus, triphenylphosphine was chosen as a precursor for dppe due to its availability and structural similarity. Na and NH<sub>3</sub>, both of which are also readily available, were chosen to perform solvated electron reduction on triphenylphosphine, which would yield the dppe ligand upon subsequent reaction with 1,2-dichloroethane (Scheme 1). The newly-synthesized dppe ligand was then reacted with NiCl<sub>2</sub> · 6 H<sub>2</sub>O to yield the polymerization catalyst Ni(dppe)Cl<sub>2</sub> (Scheme 2).

The experiment resulted in a 117.74% yield of dppe, and a 47% yield of Ni(dppe)Cl<sub>2</sub>. 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<sub>2</sub> 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.<sup>4</sup>

To further investigate these findings, the 60 MHz <sup>1</sup>H and 400 MHz <sup>31</sup>P NMR spectra taken in CDCl<sub>3</sub> were analyzed. The <sup>1</sup>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 <sup>1</sup>H NMR spectra. These are due both to the poor resolution of the 60 MHz instrument and the overlap with the solvent CDCl<sub>3</sub> 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 <sup>1</sup>H NMR spectra of dppe.<sup>5</sup>

This hypothesis is further supported by the <sup>1</sup>H NMR spectrum of Ni(dppe)Cl<sub>2</sub>, which was able to distinguish the same aromatic protons from the CDCl<sub>3</sub> shift. This is because the presence of the Ni<sup>2+</sup> metal center withdraws elec-

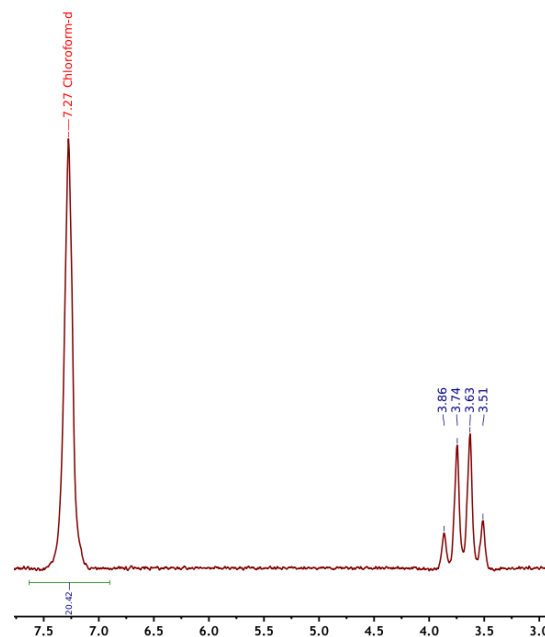


Figure 1: <sup>1</sup>H NMR of dppe, magnified to highlight the aromatic shifts at  $\delta = 7.27$  ppm (20 H). Note the overlap with the existing CDCl<sub>3</sub> peak and the diethyl ether signal ( $\delta = 3.68$  ppm, q).

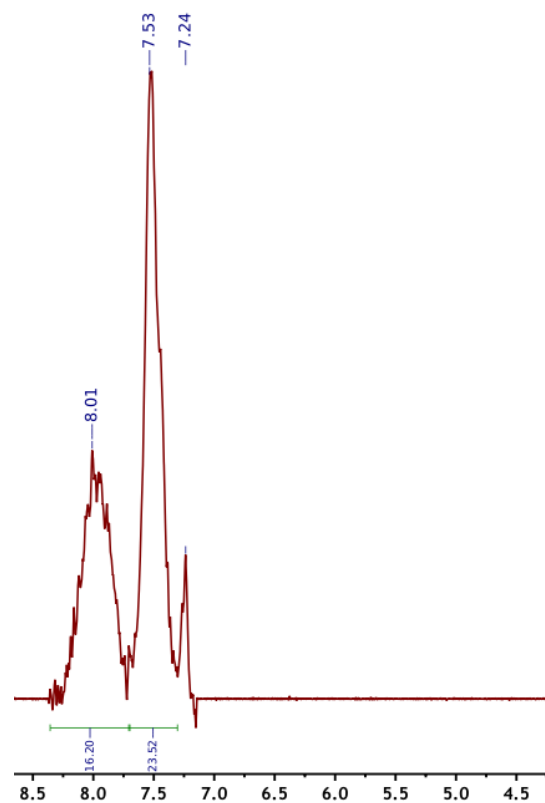


Figure 2: <sup>1</sup>H NMR of dppe, magnified to highlight the aromatic shifts at  $\delta = 8.01$  ppm (16 H) and  $\delta = 7.53$  (24 H). Note the distinguished CDCl<sub>3</sub> peak ( $\delta = 7.24$  ppm) upon formation of the nickel complex.

tron 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  $^{31}\text{P}$  NMR spectra were not particularly revealing, as there exists only one chemically distinct phosphorus atom in both dppe and  $\text{Ni}(\text{dppe})\text{Cl}_2$ . However, there was an unknown impurity at  $\delta = -105.91$  ppm and  $\delta = -221.00$  ppm observed in both  $^{31}\text{P}$  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  $^1\text{H}$  NMR multiplicities (indistinguishable due to the poor resolution), the chemical shifts of both the  $^1\text{H}$  and  $^{31}\text{P}$  spectra are in good agreement with existing studies done on dppe and  $\text{Ni}(\text{dppe})\text{Cl}_2$ .<sup>5,6</sup>

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  $\text{Ni}(\text{dppe})\text{Cl}_2$  was completely absent in the 3000-4000  $\text{cm}^{-1}$  region. This is in fact largely consistent with existing IR studies on  $\text{Ni}(\text{dppe})\text{Cl}_2$ ,<sup>7</sup> which indicate exceedingly weak C-H stretches in  $\text{Ni}(\text{dppe})\text{Cl}_2$ .

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  $\text{Ni}(\text{dppe})\text{Cl}_2$ . As indicated by the  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, and IR analysis, future studies should improve upon this synthesis by minimizing residual solvent, improving  $\text{Ni}(\text{dppe})\text{Cl}_2$  yield via temperature control, and using higher resolution NMR instruments to characterize dppe.

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