

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

David Qiu

Department of Chemistry, University of Illinois at Urbana-Champaign, 505 S Matthews Avenue, Urbana, IL, 61801

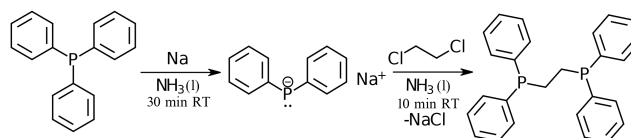
E-mail: davidlq2@illinois.edu

Abstract

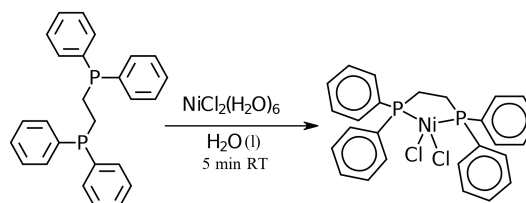
This experiment demonstrated successful synthesis of the dppe ligand via solvated electron reduction of triphenylphosphine followed by treatment with 1,2-dichloroethane. Subsequent ligand substitution of NiCl₂ · 6 H₂O yielded Ni(dppe)Cl₂. The reaction had an overall yield of 117.74% for dppe and 47% for Ni(dppe)Cl₂. ¹H NMR, ³¹P NMR, and IR spectra of dppe and Ni(dppe)Cl₂ 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 via vacuum, improving Ni(dppe)Cl₂ yield via temperature control, and using higher resolution NMR instruments to characterize dppe.

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. Cp₂ZrCl₂), 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.¹

A bulky, polydentate ligand such as dppe shares this property, making dppe complexes useful polymerization catalysts. This catalytic ability is exhibited in Ni(dppe)Cl₂, which is already known to promote chain growth and cross-coupling of aromatic molecules.²⁻⁴



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



Scheme 2: Synthesis of Ni(dppe)Cl₂ via direct ligand substitution of NiCl₂ · 6 H₂O.

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

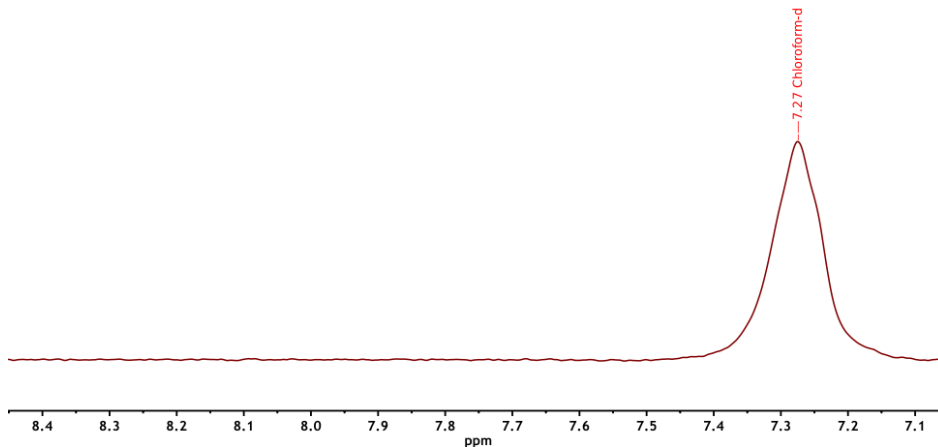


Figure 1: ^1H NMR of dppe, magnified to highlight the aromatic shifts at $\delta = 7.27$ ppm. Note the overlap with the existing CDCl_3 peak.

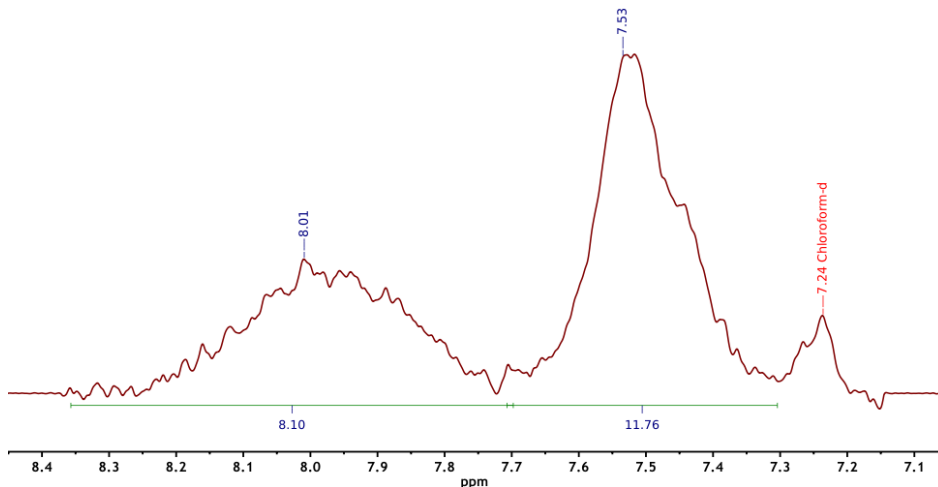


Figure 2: ^1H NMR of $\text{Ni}(\text{dppe})\text{Cl}_2$, magnified to highlight the aromatic shifts at $\delta = 8.01$ ppm (8 H) and $\delta = 7.53$ (12 H). Note the distinguished CDCl_3 peak ($\delta = 7.24$ ppm) upon formation of the nickel complex.

$\text{Ni}(\text{dppe})\text{Cl}_2$ complex for use in polymer chemistry. The synthetic route thus needed to maximize usage of readily available reagents for synthesis. Triphenylphosphine was chosen as a precursor for dppe due to its availability and structural similarity. Na and NH_3 , 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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to yield the polymerization catalyst $\text{Ni}(\text{dppe})\text{Cl}_2$ (Scheme 2).

The experiment resulted in a 117.74% yield of dppe, and a 47% yield of $\text{Ni}(\text{dppe})\text{Cl}_2$. The dppe sample thus contained some residual im-

purity or solvent, analysis of which is discussed later. The yield of $\text{Ni}(\text{dppe})\text{Cl}_2$ 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. However, this is unlikely as metal chelates are known to be highly stable.⁵ Furthermore, existing literature support the kinetic hypothesis, as yields above 90% were achieved at higher temperatures in 2-propanol.⁴

To further investigate these findings, the 60 MHz ^1H and 400 MHz ^{31}P NMR spectra in CDCl_3 were taken and analyzed. The ^1H NMR

spectrum of dppe was rather poor; ethanol was a prominent impurity, and shifts corresponding to the aromatic hydrogens were not discernible in the ^1H NMR spectra (Figure 1). These are due both to the poor resolution of the 60 MHz instrument and overlap with the CDCl_3 solvent peak.

This finding has been replicated in the literature,⁴ and is further evidenced by the ^1H NMR spectrum of $\text{Ni}(\text{dppe})\text{Cl}_2$ (Figure 2), which had distinguishable aromatic shifts unlike the ^1H NMR spectrum of dppe (c.f. Figure 1). 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. This rationale is supported by the integration underneath each aromatic peak in Figure 2, which distinguishes the 8 meta protons to the 12 ortho and para protons.

The ^{31}P NMR spectra were not particularly revealing, as there exists only one chemically distinct phosphorus nucleus in both dppe and $\text{Ni}(\text{dppe})\text{Cl}_2$. However, there was either an unknown impurity or an instrumental artifact at $\delta = -105.91$ ppm and $\delta = -221.00$ ppm observed in both ^{31}P NMR spectra of dppe and $\text{Ni}(\text{dppe})\text{Cl}_2$. This finding was not replicated elsewhere, suggesting that its corresponding impurities are unique to this synthetic method, or that the artifacts are unique to the NMR instrument used in this experiment.

Aside from the aforementioned impurities, artifacts, and ^1H NMR multiplicities (indistinguishable due to the poor resolution), the ^1H and ^{31}P spectra are in good agreement with existing NMR studies done on dppe and $\text{Ni}(\text{dppe})\text{Cl}_2$.^{4,6}

The IR spectrum of dppe was not noteworthy, and indicated exclusively a C-H stretch, an aromatic C-C/C=C stretch, and an O-H stretch corresponding to ethanol. Interestingly, the IR spectrum of $\text{Ni}(\text{dppe})\text{Cl}_2$ was completely absent in the $3000\text{--}4000\text{ cm}^{-1}$ region, and exhibited purely an aromatic C-C/C=C stretch. This is largely consistent with existing IR spectra of $\text{Ni}(\text{dppe})\text{Cl}_2$ in literature,⁷ which indicate ex-

ceedingly 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 subsequent ligand substitution to yield $\text{Ni}(\text{dppe})\text{Cl}_2$. As indicated by the ^1H NMR, ^{31}P NMR, and IR analysis, future studies should improve upon this synthesis by minimizing residual solvent (e.g. by drying the sample under vacuum prior to analysis), 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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