Supporting Information: 1,2-bis(diphenylphosphino)ethane (dppe) and $Ni(dppe)Cl_2$ synthesis via solvated electron reduction

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1 General Considerations

1.1 Instruments and Materials

^{1}H NMR spectra were taken on a 60 MHz Nanalysis NMReady-60PRO tabletop NMR instrument. ^{31}P NMR spectra were taken on a 400 MHz Varian NMR spectrometer. IR spectra were taken on a Perkin Elmer Spectrum Two FTIR spectrometer.

n-hexane, ethanol, and NH_3 were sourced from UIUC. Diethyl ether and Na were sourced from Fischer Chemical. Triphenylphosphine and 1,2-dichloroethane were sourced from Acros. NH_4Br was sourced from Oakwood Chemical.

1.2 Hazards

All organic solvents should be assumed to be acutely toxic, volatile, flammable, and irritating unless otherwise noted, and should only be used within a fume hood. NH_3 is highly volatile and flammable, is an extreme irritant to the skin and eyes, and should be used only inside a fume hood. Na is highly reactive with water, and can cause severe alkali burns of the skin and eyes if direct physical contact is made. Triphenylphosphine is acutely toxic to the nervous system. NH_4Br is a respiratory irritant. Both $NiCl_2 \cdot 6\,H_2O$ and 1,2-dichloroethane are also carcinogenic.

2 Experimental Procedures

dppe synthesis:[S1] To a 500 mL round-bottom flask was charged 200 mL of NH_3, a glass-coated stir bar. A dry ice condenser connected to a bubbler, gas inlet valve, and rubber septum were attached to the appartus. Na (2.379 g, 0.1035 mol, 4 equiv.) was added slowly over 3 minutes. A dark blue solution formed over 10 minutes, after which triphenylphosphine (13.55 g, 0.05166 mol, 2 equiv.) was added in 1 g portions. This solution was stirred for 30 minutes. NH_4Br (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 gas inlet valve was left open to air for 1 week. The dried reaction mixture was washed with DI water and rotary evaporated following dilution with ethanol. The purified, milky-white dppe powder precipitated, and was filtered out of solution and washed with ethanol.

The reaction recorded a percent yield of 118% (12.11 g total, 10.29 g expected). The ^{1}H NMR spectrum interpretation is as follows (60 MHz, δ): 7.27 ppm, 2.06 ppm (4 H, t). The ^{31}P NMR spectrum interpretation is as follows (400 MHz, δ): -11.52 ppm (s). The IR spectrum interpretation is as follows ($\tilde{\nu}$): 2950 cm^{-1} (C–H stretch), 1400 cm^{-1} (aromatic C–C/C=C stretch). Aside from the presence of identified impurities and ^{31}P NMR instrument artifacts, the ^{1}H NMR, ^{31}P NMR, and IR spectra are in excellent agreement with literature values.[S2,S3]

Ni(dppe)Cl$_2$ synthesis:[S1] $NiCl_2 \cdot 6\,H_2O$ (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. The tomato-red Ni(dppe)Cl$_2$ precipitate was filtered out and washed with diethyl ether.

The reaction recorded a percent yield of 47% (0.33 g total, 0.71 g expected). The ^{1}H NMR spectrum interpretation is as follows (60 MHz, δ): 8.01 ppm (8 H, meta), 7.53 ppm (12 H, ortho/para), 2.12 ppm (4 H, ethane bridge). The ^{31}P NMR spectrum interpretation is as follows (400 MHz, δ): -58.23 ppm (s). The IR spectrum interpretation is as follows ($\tilde{\nu}$): 1450 cm^{-1} (aromatic C–C/C=C stretch). Aside from presence of identified impurities ^{31}P NMR instrument artifacts, the ^{1}H NMR, ^{31}P NMR, and IR spectra are in excellent agreement with literature values.[S2–S4]

3 ^{1}H NMR Spectra

3.1 ^{1}H NMR spectrum of dppe

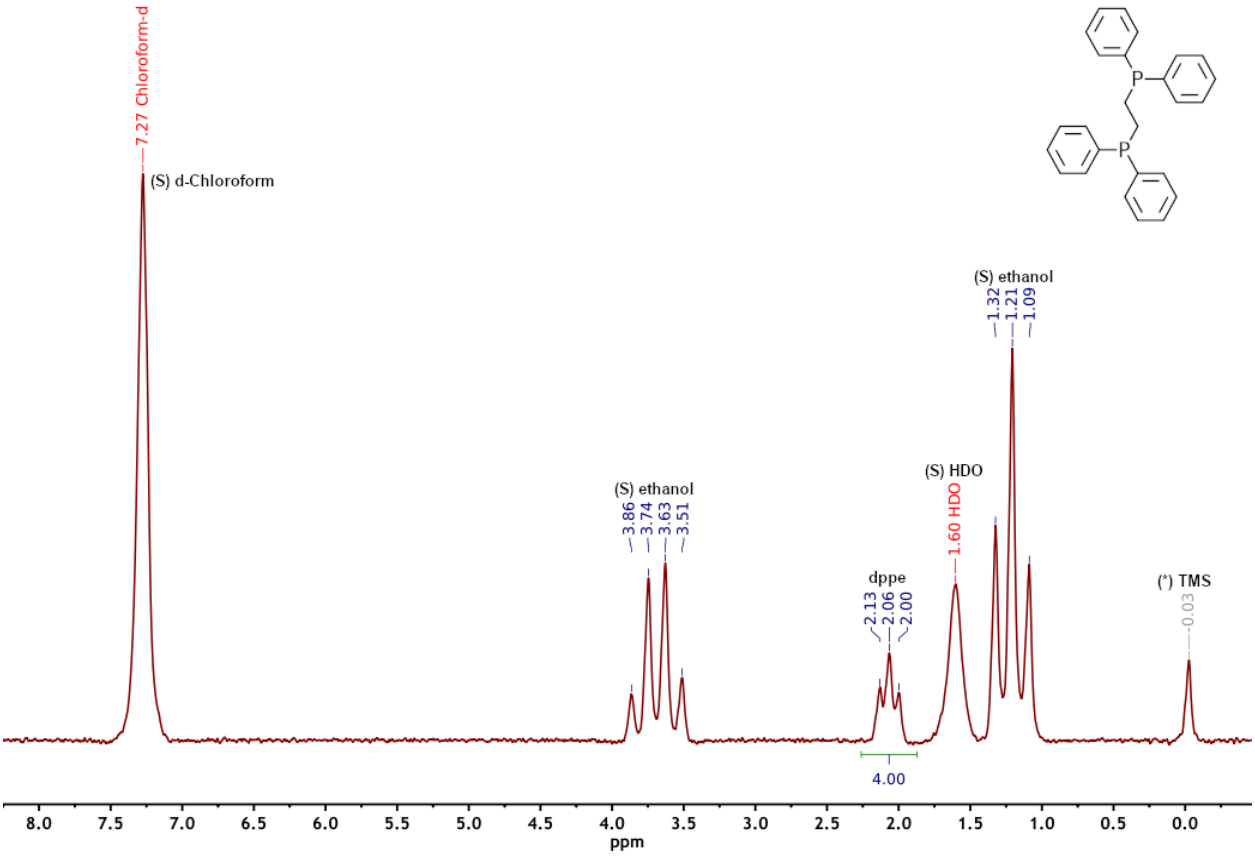

Figure S1: 60 MHz ^{1}H NMR spectrum of dppe. The impurities are listed as follows (δ):[S5] 7.27 ppm ($CDCl_3$, s), 3.58 ppm (ethanol, q), 1.21 ppm (ethanol, t), 1.60 ppm (HDO, s), −0.03 ppm (TMS, s).

3.2 ^{1}H NMR spectrum of Ni(dppe)Cl_2

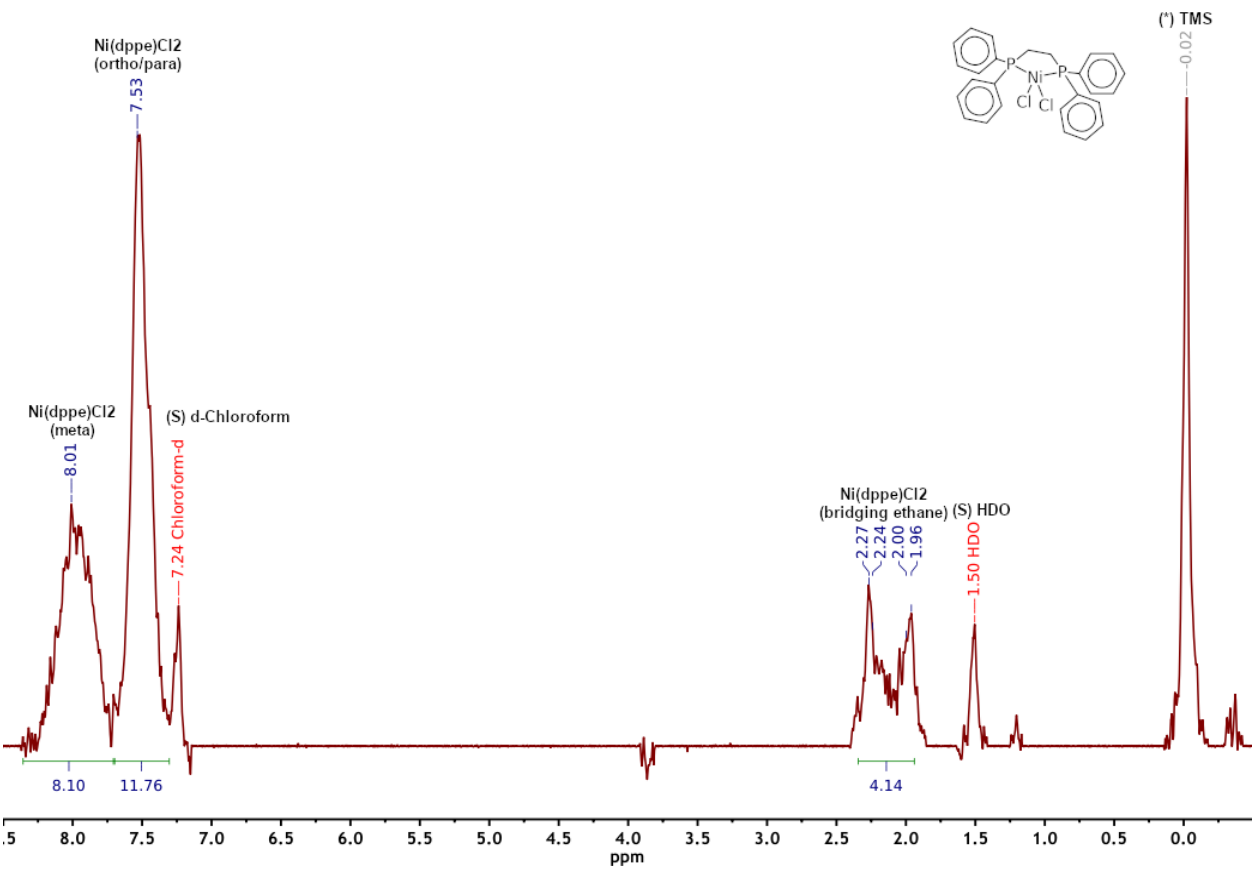

Figure S2: 60 MHz ^{1}H NMR spectrum of Ni(dppe)Cl_2. The impurities are listed as follows (δ):[S5] 7.24 ppm ($CDCl_3$, s), 1.50 ppm (HDO, s), −0.02 ppm (TMS, s).

4 ^{31}P NMR Spectra

4.1 ^{31}P NMR spectrum of dppe

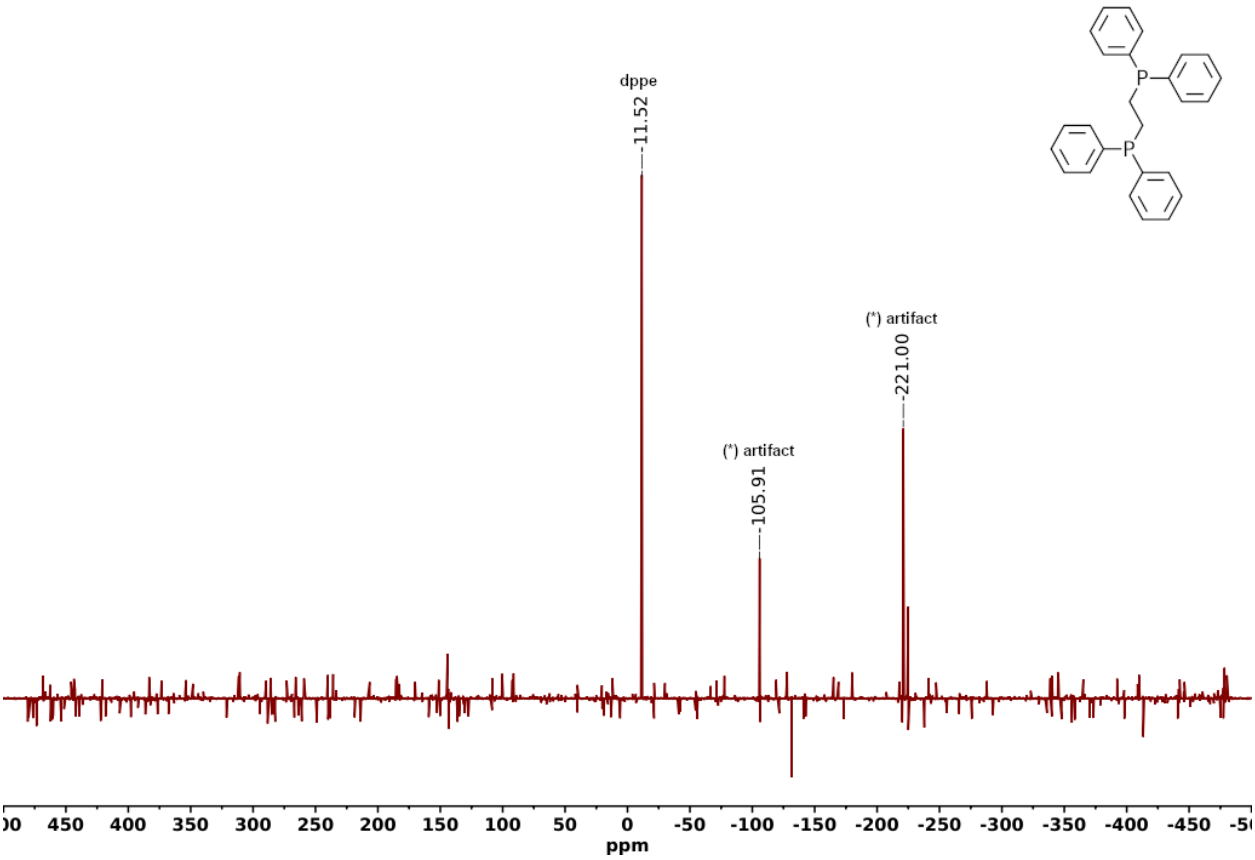

Figure S3: 400 MHz ^{31}P NMR spectrum of dppe. Note the instrument artifacts at −105.91 ppm and −221.00 ppm.

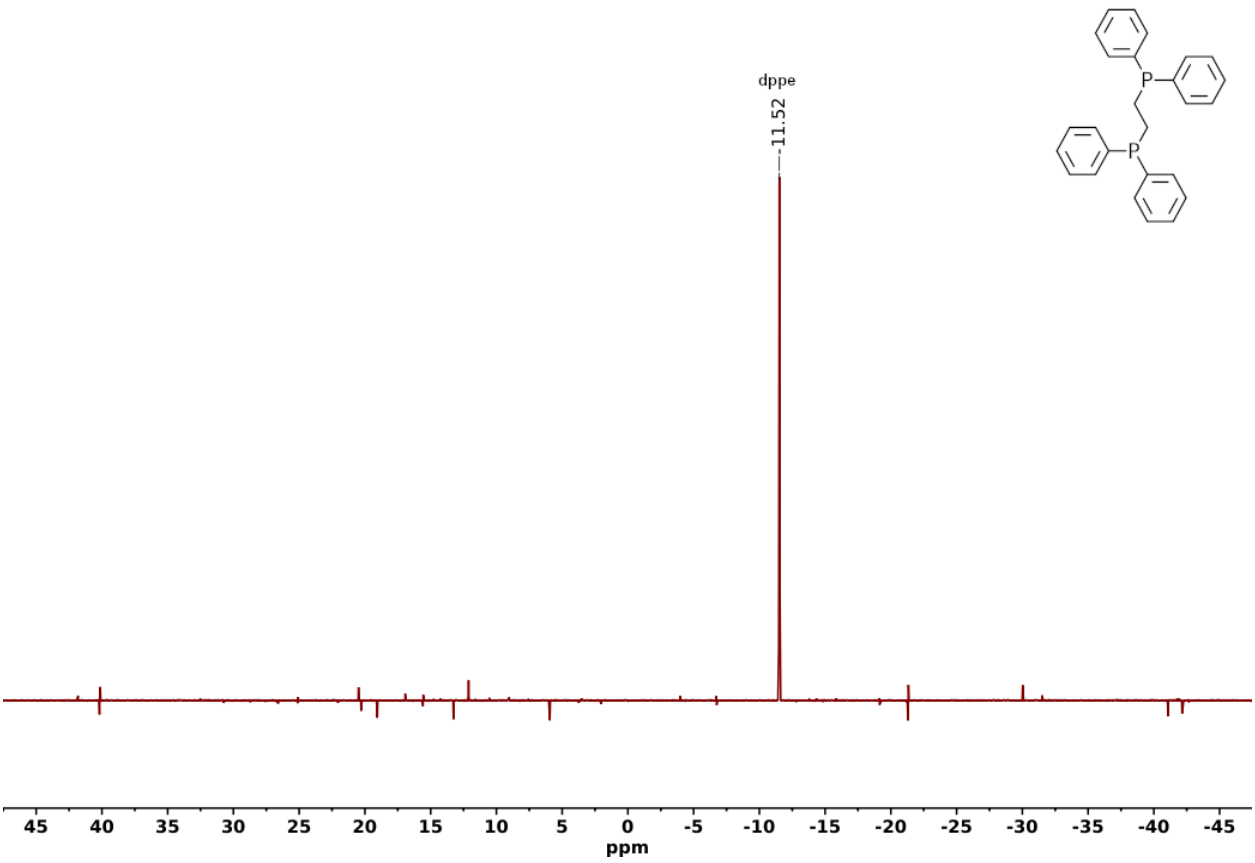

Figure S4: 400 MHz ^{31}P NMR spectrum of dppe, enhanced near the product peak.

4.2 ^{31}P NMR spectrum of Ni(dppe)Cl$_2$

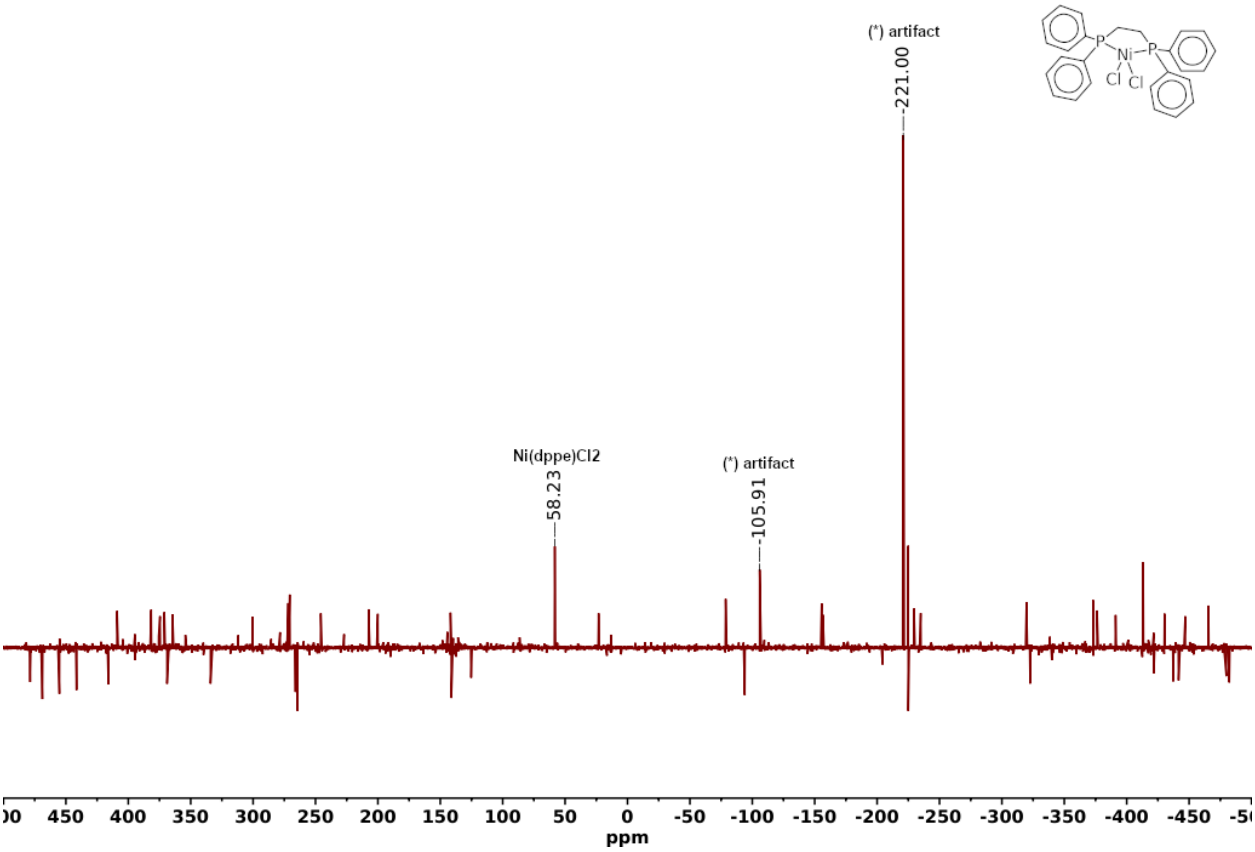

Figure S5: 400 MHz ^{31}P NMR spectrum of Ni(dppe)Cl$_2$. Note the instrument artifacts at −105.91 ppm and −221.00 ppm.

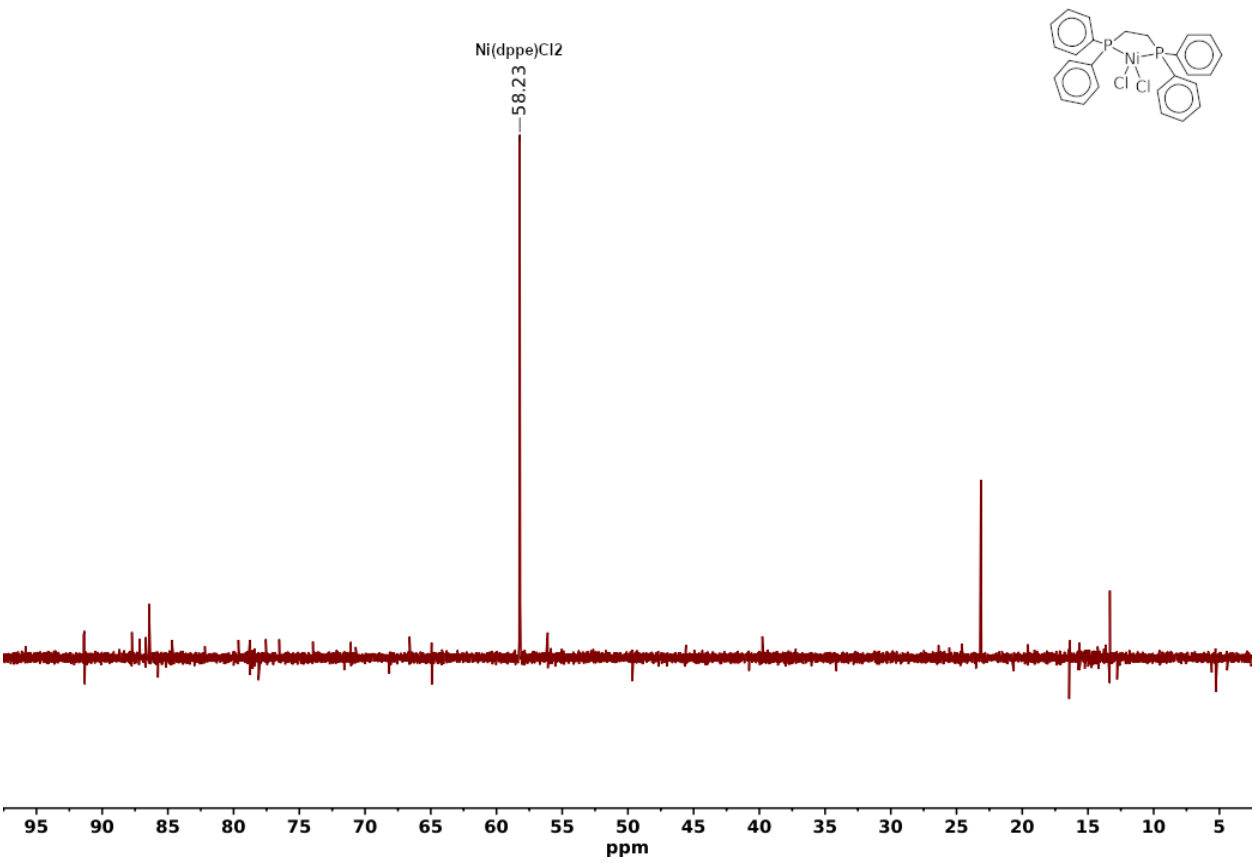

Figure S6: 400 MHz ^{31}P NMR spectrum of Ni(dppe)Cl_2, enhanced near the product peak.

5 IR Spectra

5.1 IR spectrum of dppe

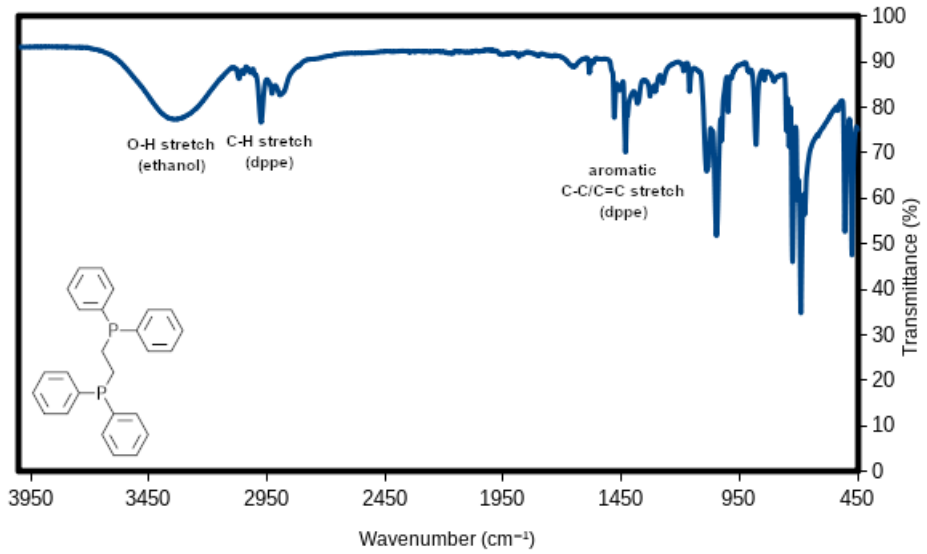

Figure S7: IR spectrum of dppe. Note the presence of ethanol ($\tilde{\nu} = 3300$ cm^{-1}).

5.2 IR spectrum of Ni(dppe)Cl_2

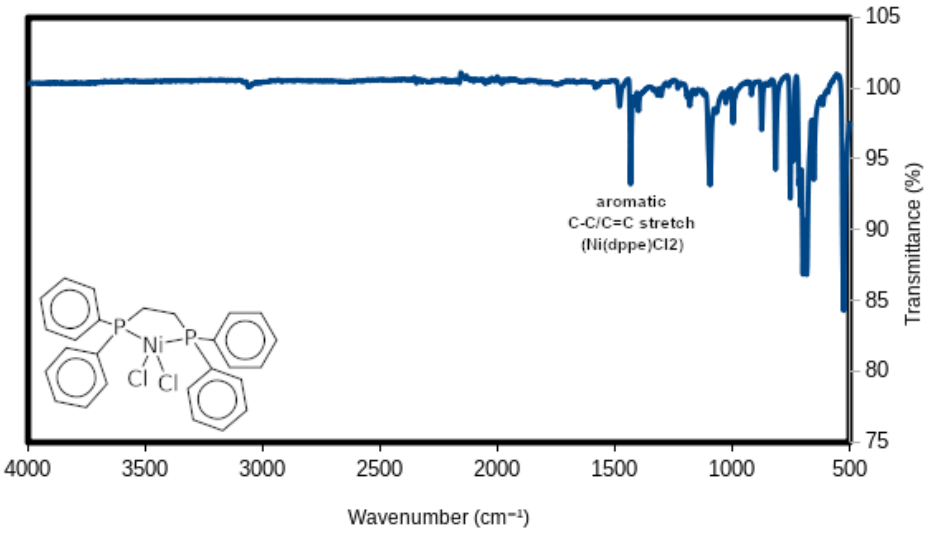

Figure S8: IR spectrum of Ni(dppe)Cl_2.

References

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(S4) Benial, A. M. F.; Ramakrishnan, V.; Murugesan, R. Infrared and laser Raman studies of [Ni(II)(dppe)Cl2] and [Co(III)(dppe)2Cl2]PF6 (dppe=1,2-bis(diphenylphosphino)ethane). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2002**, *58*, 1703–1712.

(S5) Fulmer, G. R.; Miller, A. J.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR chemical shifts of trace impurities: common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist. *Organometallics* **2010**, *29*, 2176–2179.