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}H NMR spectra were taken on a 60 MHz Nanalysis NMReady-60PRO tabletop NMR instrument coupled with a STC-1000 digital temperature controller. ^{31}P NMR spectra were

taken on a 400 MHz Varian NMR spectrometer. IR spectra were taken on a Perkin Elmder Spectrum Two FTIR spectrometer.

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

2 Experimental Procedures

dppe synthesis:[S1] 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_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 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:[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, 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.

^{1}H and ^{31}P NMR: ^{1}H and ^{31}P NMR were taken, and the results were as follows. (*) denotes an unidentified impurity.

In the dppe NMR spectrum: ^{1}H: $\delta = 7.27$ ppm (20 H), $\delta = 2.06$ ppm (4 H, t), $\delta = 3.58$ ppm (diethyl ether,[S2] q), $\delta = 1.21$ ppm (diethyl ether,[S2] t), $\delta = 1.60$ ppm (HDO,[S2] s). ^{31}P:

δ = -11.52 ppm (dppe), δ = -105.91 ppm (*), δ = -221.00 ppm (*).

In the Ni(dppe)Cl_2 NMR spectrum: ^{1}H: δ = 8.01 ppm (16 H), δ = 7.53 ppm (24 H), δ = 7.24 ppm ($CDCl_3$), δ = 2.12 ppm (8 H), δ = 1.50 ppm (HDO). $^{31}P^{31}P$: δ = 58.23 ppm (Ni(dppe)Cl_2), δ = -105.91 ppm (*), δ = -221.00 ppm (*).

In the dppe IR spectrum: ν = 3300 cm^{-1} (O-H), ν = 2950 cm^{-1} (C-H).

3 NMR and IR Spectra

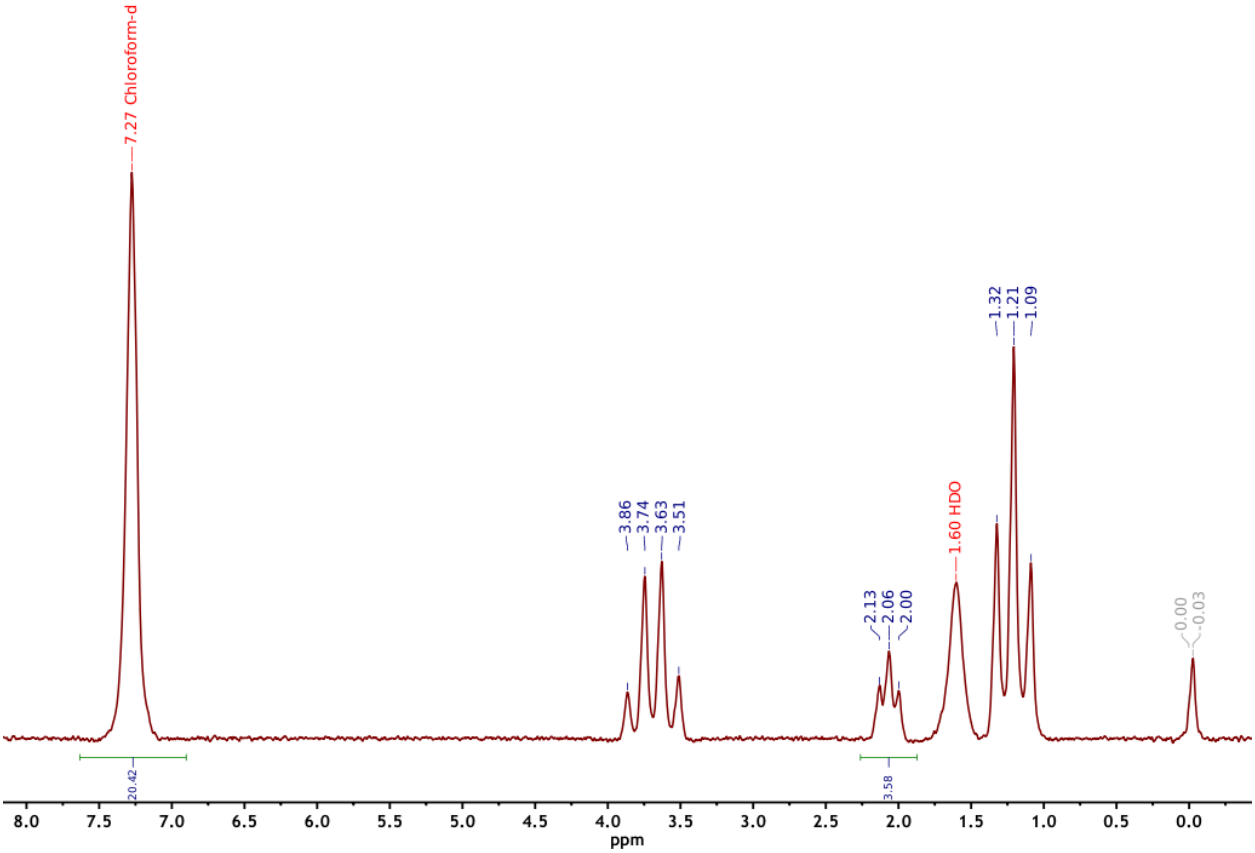

Figure S1: ^{1}H NMR spectrum of dppe.

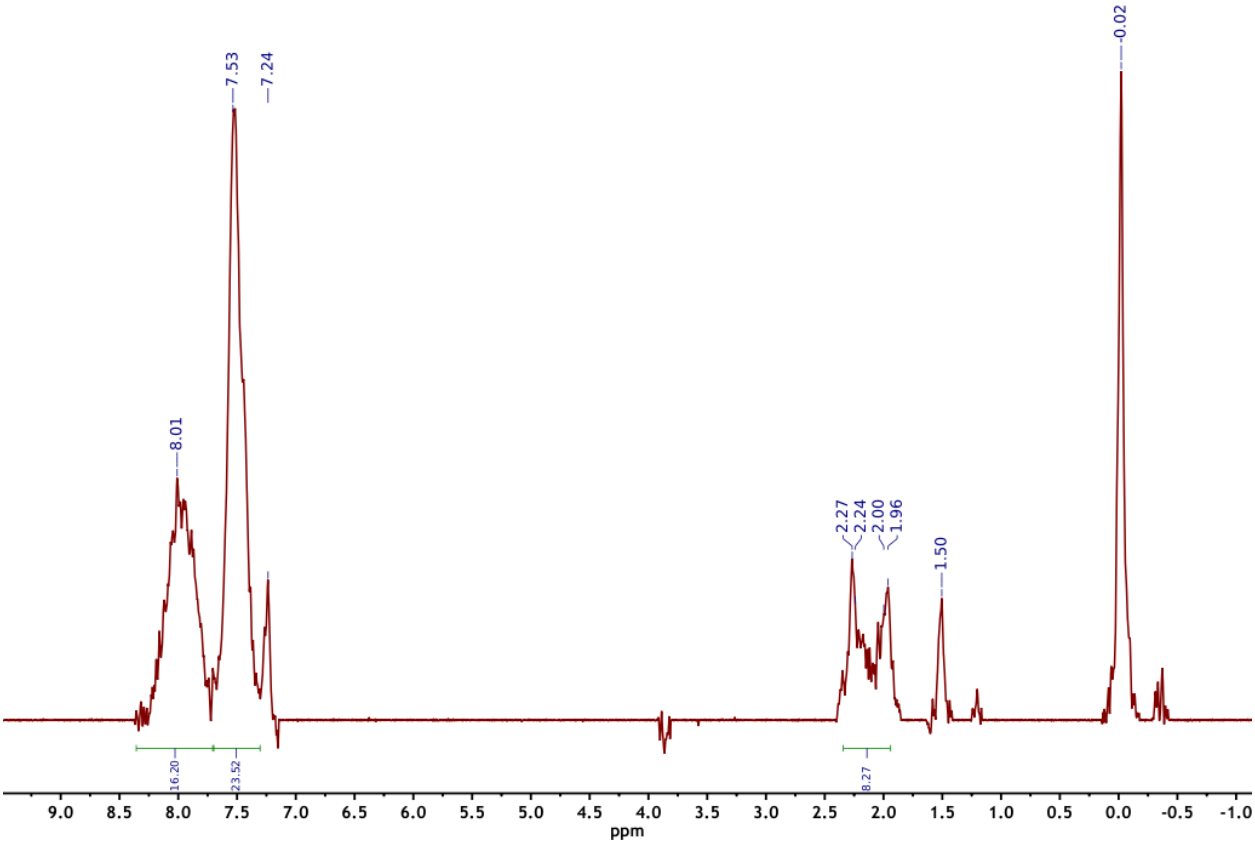

Figure S2: ^{1}H NMR spectrum of Ni(dppe)Cl_2.

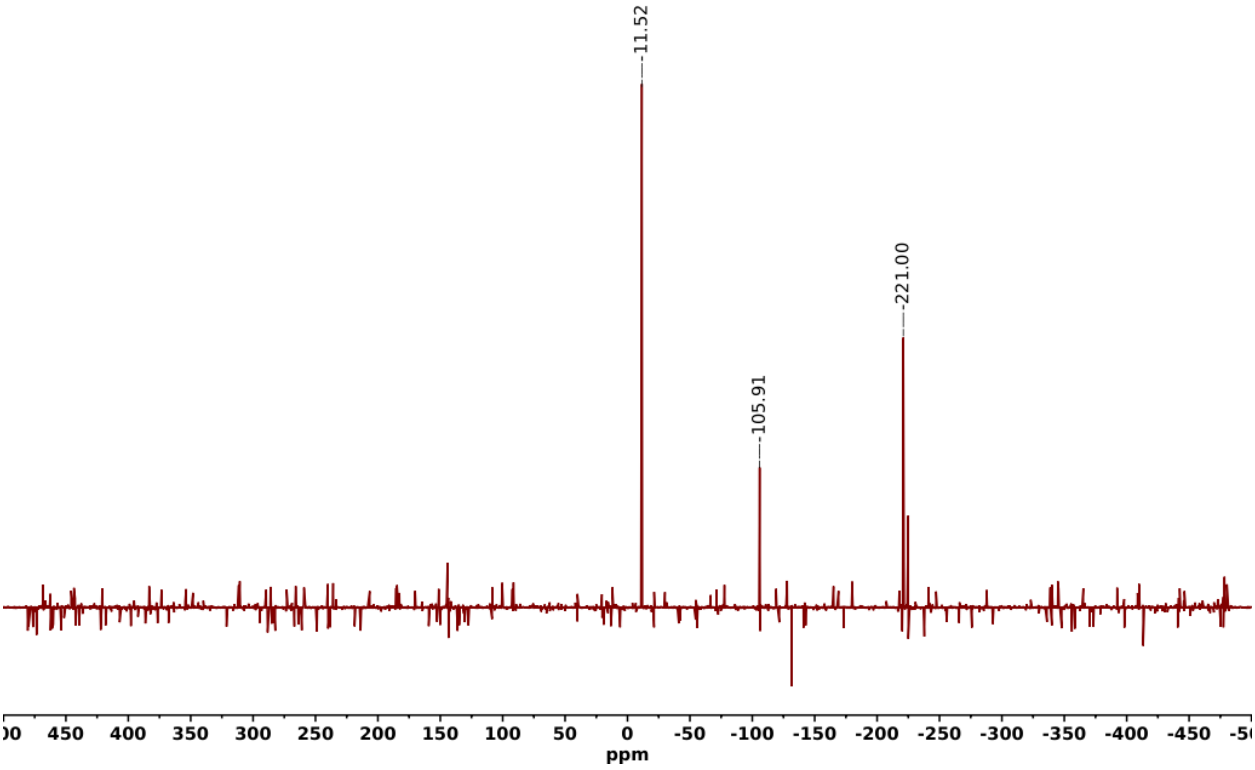

Figure S3: ^{31}P NMR spectrum of dppe.

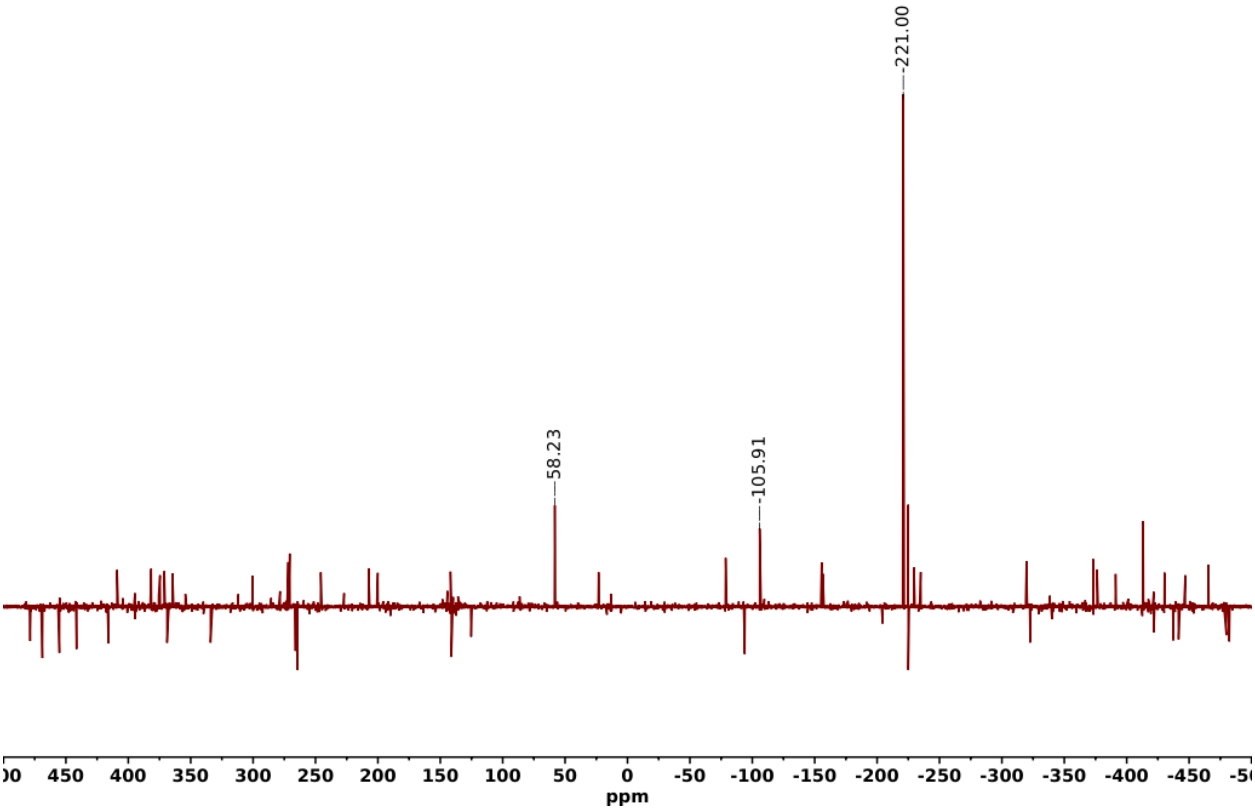

Figure S4: ^{31}P NMR spectrum of Ni(dppe)Cl_2.

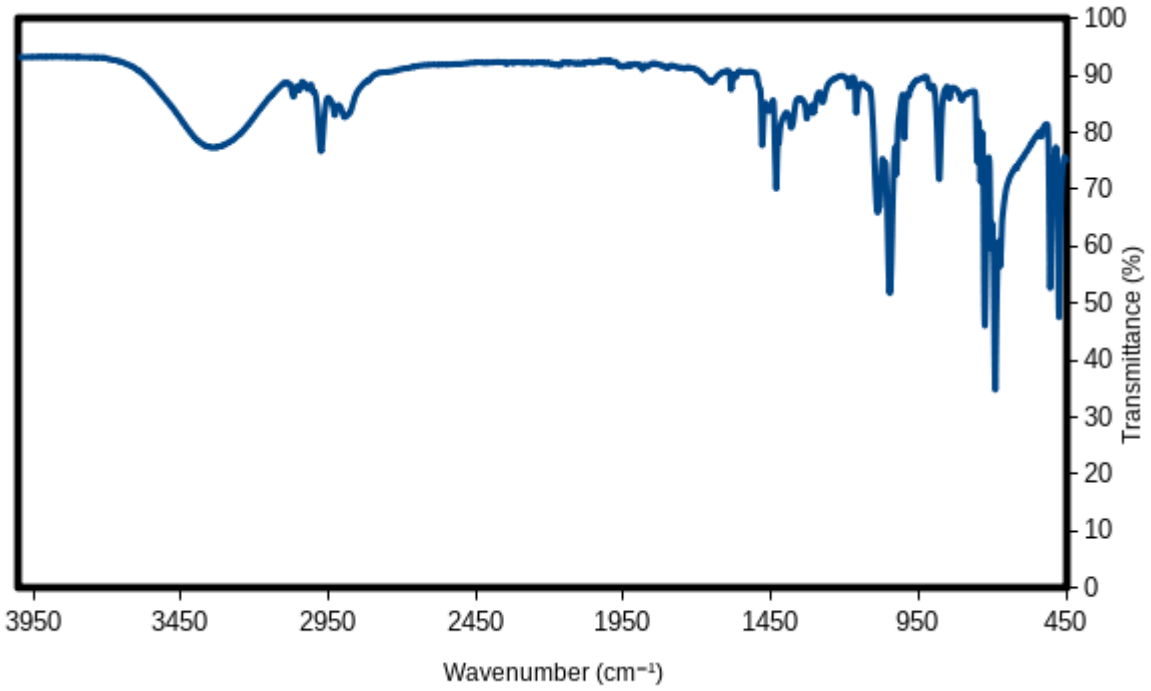

Figure S5: IR spectrum of dppe.

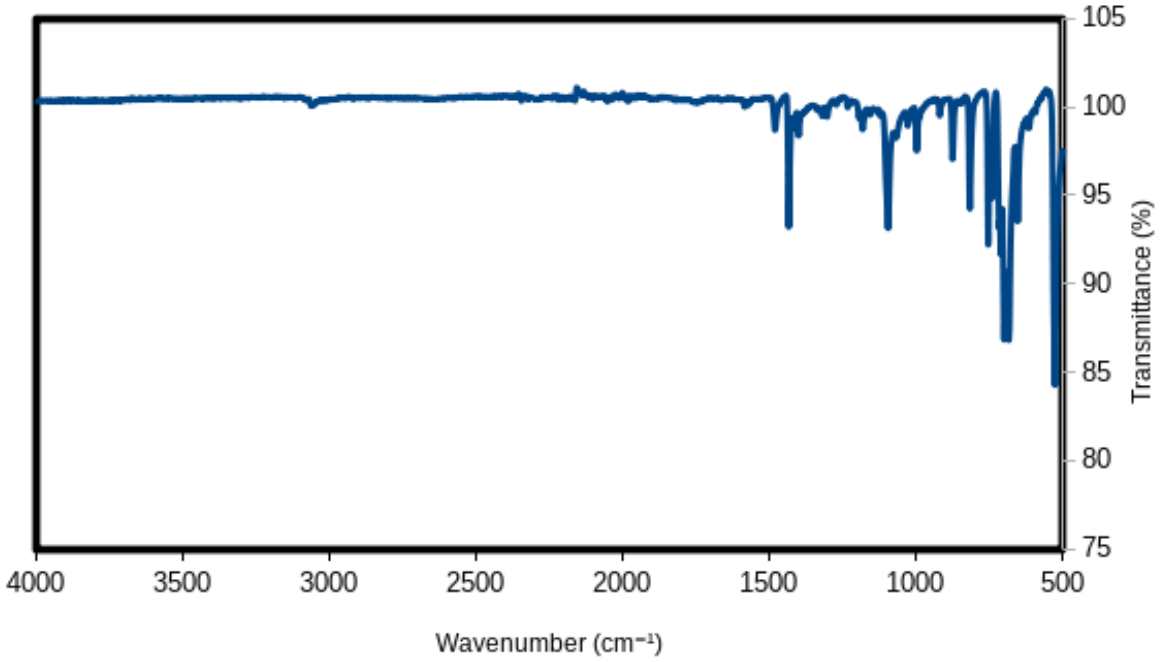

Figure S6: IR spectrum of Ni(dppe)Cl_2.

References

(S1) Girolami, G. S.; Rauchfuss, T. B.; Angelici, R. J. *Synthesis and Techniques in Inorganic Chemistry*, 3rd ed.; University Science Books, 1999.

(S2) 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.