

# Supporting Information:

## Synthesis of nickelocene via ligand substitution of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$

David Qiu

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

E-mail: davidlq2@illinois.edu

### Contents

<b>1</b>	<b>General Considerations</b>	<b>S-2</b>
<b>2</b>	<b>Experimental</b>	<b>S-2</b>
2.1	$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ synthesis . . . . .	S-2
2.2	$\text{Ni}(\text{Cp})_2$ synthesis . . . . .	S-2
2.3	$\text{Ni}(\text{Cp})_2$ sublimation and analysis . . . . .	S-3
<b>3</b>	<b><math>^1\text{H}</math> NMR Spectrum</b>	<b>S-4</b>
<b>4</b>	<b>IR Spectrum</b>	<b>S-5</b>
	<b>References</b>	<b>S-5</b>

# 1 General Considerations

Throughout the experiment, a 60 MHz Nanalysis NMReady-60PRO tabletop NMR instrument was used to record all  $^1\text{H}$  NMR spectra at room temperature. NMR spectrum was sourced from a fellow classmate. IR spectra were taken on a Perkin Elmer Spectrum Two FTIR spectrometer. The experiment was performed according to Girolami et al.<sup>S1</sup>

Diethyl ether was sourced from Fischer Chemical. Ammonium hydroxide (28.0%–30.0%  $\text{NH}_3$ ) was sourced from Macron Fine Chemicals.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and NaCp (2.4 M in THF) was sourced from Sigma-Aldrich. Ethanol and THF sourced directly from the University of Urbana-Champaign Chemistry department.

## 2 Experimental

**2.1  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  synthesis**  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (8 g, 34 mmol) was mixed with 20 mL DI water in a flask. While stirring, 30 mL of concentrated ammonium hydroxide (28.0%–30.0%  $\text{NH}_3$ ) was poured in, forming a cloudy purple mixture. This solution was cooled in an ice bath, and 80 mL of ethanol was added. The  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  precipitate was filtered through a coarse glass frit, and was washed with ethanol and diethyl ether. The  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  was then dried, yielding a percent yield of 85.5% (6.74 g total, 7.88 g expected).

**2.2  $\text{Ni}(\text{Cp})_2$  synthesis**  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  (1.2 g, 5 mmol) and a stir bar was added to a three-necked round-bottom flask placed in an ice bath. A gas inlet valve, glass stopper, and rubber septum were attached, and the flask was filled with  $\text{N}_2$  on a Schlenk line. 20 mL of THF was injected, and 5 mL of NaCp was added drop-wise. This was allowed to react for 1 hour, during which the solution turned a dark brown. The reaction was quenched with 1 mL of ethanol. Residual solvent was removed via the Schlenk line. The rubber stopper was quickly replaced with a glass stopper, and all joints were re-greased.

**2.3 Ni(Cp)<sub>2</sub> sublimation and analysis** A cold finger was quickly fitted to the central neck of the Ni(Cp)<sub>2</sub> flask, and the flask was placed under a static vacuum. The flask was then heated via a heating mantle between 80–120 °C (40 V on a Variac), and green crystals gradually formed on the cold finger over an hour. The flask was then refilled with N<sub>2</sub>, and the sublimed Ni(Cp)<sub>2</sub> crystals were then weighed, yielding a percent yield of 10.6% (0.10 g total, 0.94 g expected). <sup>1</sup>H NMR and IR spectrum were collected.

<sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>): 7.21 ppm (CHCl<sub>3</sub>, s), 2.20 ppm (acetone, s), 1.35 ppm (H grease, m), 0.12 ppm (unidentified impurity). Impurities were identified according to a table of trace impurities.<sup>S2</sup> The Ni(Cp)<sub>2</sub> product shift was not observed in the <sup>1</sup>H NMR. This interpretation is in good agreement with the literature value of the <sup>1</sup>H NMR shift of nickelocene (254.8 ppm).<sup>S3</sup>

IR:  $\tilde{\nu}$  = 2963 cm<sup>-1</sup>(C-H stretch),  $\tilde{\nu}$  = 1422 cm<sup>-1</sup>(asymmetric aromatic C-C stretch),  $\tilde{\nu}$  = 1259 cm<sup>-1</sup>(C-H bend/rock). This is in good agreement with the literature nickelocene IR spectra, which cite additional vibrational modes of the cyclopentadienyl ligand in the fingerprint region.<sup>S3,S4</sup>

### 3 $^1\text{H}$ NMR Spectrum

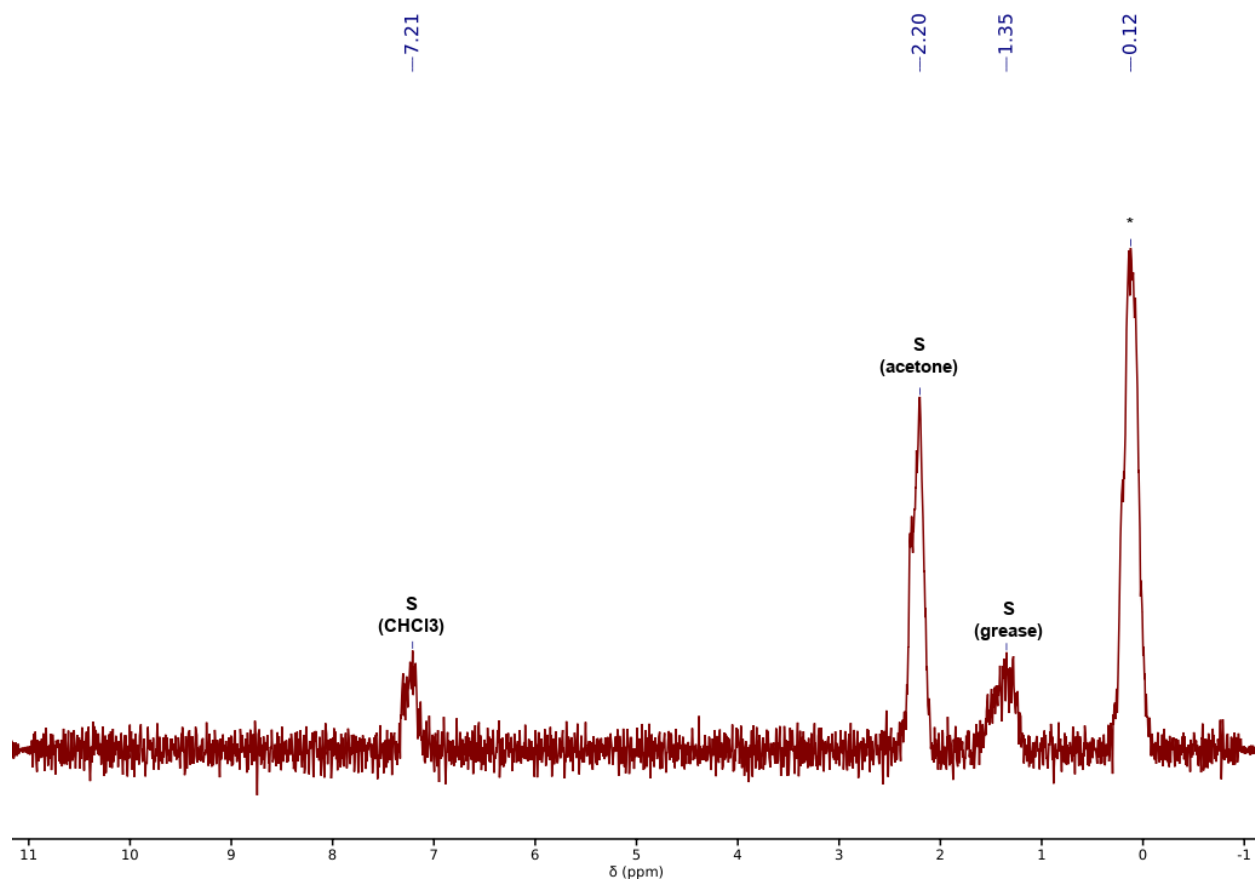


Figure S1: Provided  $^1\text{H}$  NMR spectrum of  $\text{Ni}(\text{Cp})_2$ , following baseline and phase correction. "S" denotes residual non-deuterated organic solvents, and "\*" denotes an unidentified impurity.

## 4 IR Spectrum

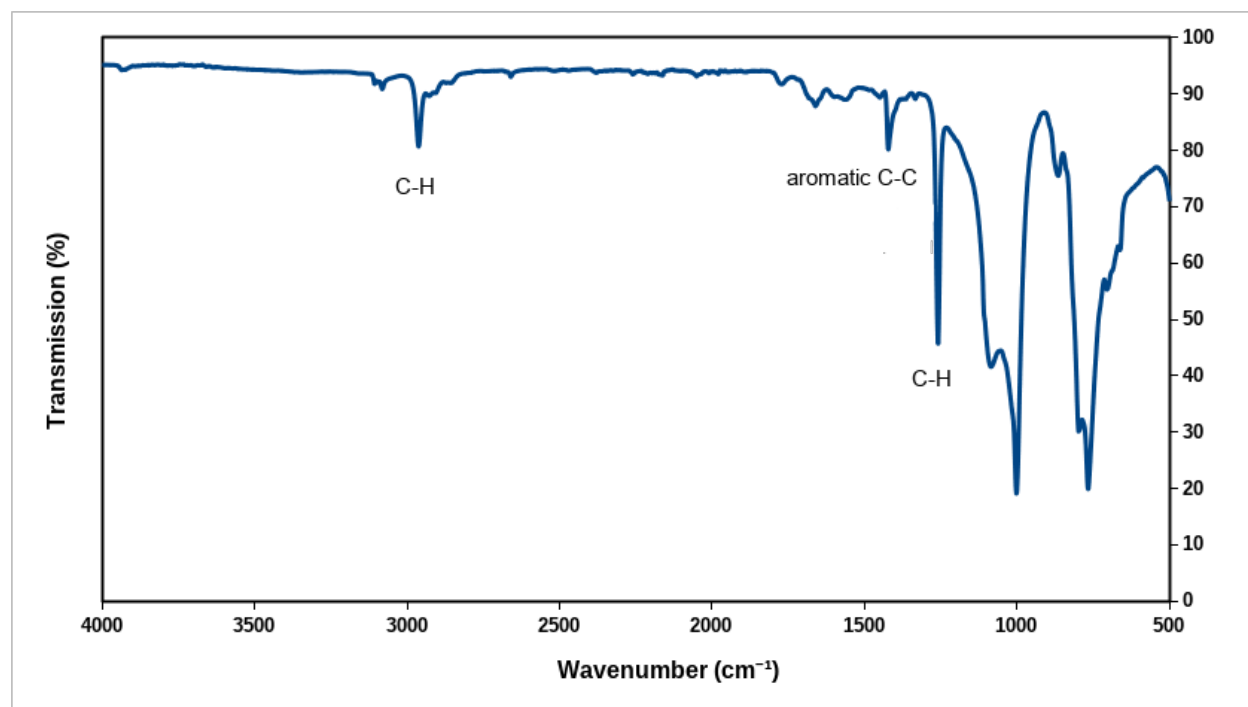


Figure S2: IR spectrum of Ni(Cp)<sub>2</sub>, with corresponding assignments.

## 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.
- (S3) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; 1974; Vol. I: Organonickel Complexes; Chapter VIII: Cyclopentadienyl Nickel Complexes.

- (S4) Wilkinson, G.; Pauson, P.; Cotton, F. Bis-cyclopentadienyl Compounds of Nickel and Cobalt. *Journal of the American Chemical Society* **1954**, 76, 1970–1974.