Video Article

Accessing Valuable Ligand Supports for Transition Metals: A Modified, Intermediate Scale Preparation of 1,2,3,4,5-Pentamethylcyclopentadiene

Zachary Call[1], Meagan Suchewski[1], Christopher A. Bradley[1]

[1]Department of Science, Mount St. Mary's University

Correspondence to: Christopher A. Bradley at cbradley@msmary.edu

URL: https://www.jove.com/video/55366
DOI: doi:10.3791/55366

Keywords: Chemistry, Issue 121, Cp*H, Iridium, Ligand, Pentamethylcyclopentadiene, Ruthenium, Synthesis, Transition Metals

Date Published: 3/20/2017

Citation: Call, Z., Suchewski, M., Bradley, C.A. Accessing Valuable Ligand Supports for Transition Metals: A Modified, Intermediate Scale Preparation of 1,2,3,4,5-Pentamethylcyclopentadiene. *J. Vis. Exp.* (121), e55366, doi:10.3791/55366 (2017).

Abstract

A reliable, intermediate scale preparation of 1,2,3,4,5-pentamethylcyclopentadiene (Cp*H) is presented, based on modifications of existing protocols that derive from initial 2-bromo-2-butene lithiation followed by acid mediated dienol cyclization. The revised synthesis and purification of the ligand avoids the use of mechanical stirring while still permitting access to significant quantities (39 g) of Cp*H in good yield (58%). The procedure offers other additional benefits, including a more controlled quench of excess lithium during the production of the intermediate heptadienols and a simplified isolation of Cp*H of sufficient purity for metallation with transition metals. The ligand was subsequently used to synthesize $[Cp^*MCl_2]_2$ complexes of both iridium and ruthenium to demonstrate the utility of the Cp*H prepared and purified by our method. The procedure outlined herein affords substantial quantities of a ubiquitous ancillary ligand support used in organometallic chemistry while minimizing the need for specialized laboratory equipment, thus providing a simpler and more accessible entry point into the chemistry of 1,2,3,4,5-pentamethylcyclopentadiene.

Video Link

The video component of this article can be found at https://www.jove.com/video/55366/

Introduction

Since the discovery and structural elucidation of ferrocene in the 1950s,[1,2,3,4] cyclopentadienyl (Cp) substituted ligands have played a vital role in the development of organometallic chemistry. These ligands have served as versatile ancillary supports for a range of metals, leading to studies of unusual structure and bonding,[5,6,7] the activation and functionalization of small molecules,[8,9,10,11,12,13] and catalysis, including olefin polymerization.[14,15]

The 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) anion has proven to be a particularly valuable ligand in transition and main group metal chemistry, as the methyl groups impart greater steric protection, increased electron donation by the anionic ligand, and block potential activation of the cyclopentadienyl ring.[16,17] The Cp* ligand remains relevant even today, as the anion has recently been utilized to support H/D exchange by Ir(III),[18] hydride transfer by Rh,[19] and conjugate aminations mediated by Ti(III).[20]

Our interest in the Cp* ligand stems from the desire to access reactive sources of cobalt(I) for use in small molecule activation.[21] These studies have resulted in the generation of both Cp^*Co^I and Cp^*Co^IL (L = N-heterocyclic carbene) equivalents for use in sp^3 and sp^2 C-H bond oxidative addition.[22,23,24] As access to our Cp*Co(II) starting materials necessitate significant quantities of 1,2,3,4,5-pentamethylcyclopentadiene, we desired a multigram synthesis of Cp*H, given the substantial commercial cost of the ligand.

Two major methods currently exist for the large scale preparation of Cp*H, each of which presents inherent technical challenges. A procedure developed by Marks and coworkers involves a two-step synthesis of 2,3,4,5-tetramethylcyclopent-2-enone followed by installation of the final methyl group using methyl lithium.[25] The synthesis is described on a massive scale, using a 12 L reaction vessel and mechanical stirring, while also requiring sustained low temperature cooling at 0 °C for four days.

An alternative procedure originally developed by Bercaw and coworkers,[26] and later adapted by Marks,[27] utilizes *in situ* generation of an alkenyl lithium for nucleophilic attack of ethyl acetate to produce an isomeric mixture of 3,4,5-trimethyl-2,5-heptadien-4-ols followed by acid mediated cyclization to provide Cp*H. The initial reports of this method were performed on a large (3-5 L) scale and required mechanical stirring. In addition, a significant excess of lithium metal was used, complicating quenching and subsequent workup of the intermediate heptadienols. A subsequent revision of the procedure scales down the reaction and the amount of lithium,[28] but safe quenching of the reaction mixture remains an issue. Reproducibility in the initiation of the alkenyl lithium, due to differences in lithium source and purity or dryness of the 2-bromo-2-butene reactant are further noted concerns. Given these issues with the commonly used procedures for preparing Cp*H, we looked to develop better access to the ligand on an intermediate scale (30-40 g) which would circumvent use of specialty laboratory glassware and equipment, improve reaction reproducibility and safety, and simplify workup and ligand purification.

Here we report that synthesis of 1,2,3,4,5-pentamethylcyclopentadiene, based on modifications of the existing procedure developed by Bercaw and coworkers. The revised synthesis and purification of the ligand accomplishes the major goals outlined above, while permitting access to substantial amounts (39 g) of Cp*H in good yield (58%). The procedure offers other additional benefits, including a more controlled quench of excess lithium during the production of the intermediate heptadienols and a simplified isolation of Cp*H of adequate purity for subsequent metallation with transition metals. To demonstrate the utility of the prepared ligand, it was used to synthesize two $[Cp^*MCl_2]_2$ (M = Ir, Ru) complexes. The revised protocol outlined below complements existing procedures and provides a simpler and more accessible entry point into the chemistry of a ubiquitous ancillary ligand support in organometallic chemistry.

Protocol

1. Synthesis of an Isomeric Mixture of 3,4,5-Trimethyl-2,5-heptadien-4-ols

1. **Fill an oven dried, 500 mL beaker with 200 mL of hexanes and cover with an oven dried watch glass.**
    1. In an empty hood, use clean scissors to cut half inch pieces of lithium wire. Wipe each lithium piece on a paper towel to remove excess mineral oil, until all oil appears to be removed from the metal's surface, and place in the beaker containing hexanes.
    2. Fill an oven dried, 250 mL beaker with 100 mL of hexanes and cover with an oven dried watch glass. Tare this setup on a balance.
    3. Using oven dried tongs, remove the lithium wire from the first beaker, wipe quickly on a clean paper towel to remove any residual oil or hexanes, and transfer to the tared beaker. Repeat this process until 14.0 g (2.03 mol) of lithium wire have been added to the beaker.

2. **Attach an oven-dried, 1 L three-neck flask equipped with a stir bar to a Schlenk line under a flow of argon in a fume hood. Heat gun the flask for a few minutes and allow it to cool under argon.**
    Caution: It is important to use argon to prevent a potential reaction between lithium and dinitrogen to form lithium nitride.
    1. Once cooled, use tongs to quickly wipe the lithium pieces on a paper towel and then transfer the lithium into the flask under an argon counter flow.
    2. Submerge any excess lithium strips in mineral oil for storage. Rinse the tongs and scissors with copious amounts of water in an empty sink. Dry each with a paper towel and submerge the towels in water in the sink.
        NOTE: No solvent bottles or paper towels should be near the sink.
        1. Immerse any paper towels or gloves that have been used to cut lithium in a half-filled bowl of water and place in an empty sink. In an empty hood, slowly pour the hexanes from the beakers in 1.1-1.1.3 into a bowl containing water. Add water carefully into the empty beakers to quench any residual lithium.
        2. Rinse and wipe down the hood where the lithium was cut with water before continuing with the rest of the procedure. Submerge these paper towels in water in the sink before continuing.
    3. Add approximately 500 mL of diethyl ether, collected directly from a solvent purification system, to the reaction flask via cannula transfer.
    4. Attach an oven dried reflux condenser, an addition funnel equipped with an inert gas sidearm, and a glass stopper to the three neck flask. Place a plastic bowl underneath the reaction setup in case of flask rupture.
    5. Add 2-bromo-2-butene (29.0 g, 0.218 mol), which has been dried over 4 Å molecular sieves overnight, to the addition funnel via syringe.
    6. Add approximately 3-4 mL of the 2-bromo-2-butene dropwise over the course of 5 minutes to initiate the reaction, whereupon reflux occurs and the solution becomes cloudy. If gentle reflux does not occur on its own after 10-15 minutes of stirring, then warm the flask *gently* with a heat gun for two-three minutes until reflux is achieved. This is usually adequate to initiate the reaction.
        Caution: Even if the reaction does not initiate immediately, controlled addition of 2-bromo-2-butene is critical to keep the reaction under control.
    7. Add the remainder of the 2-bromo-2-butene in the addition funnel dropwise over the course of 90 minutes at a rate that maintains moderate reflux throughout the time period. The reaction mixture will turn a light green color.
    8. Syringe a mixture of ethyl acetate (40.0 g, 0.454 mol), which has been dried over 4 Å molecular sieves overnight, and 2-bromo-2-butene (103.85 g, 0.782 mol) into the addition funnel. Add this mixture to the reaction at a sufficient rate to maintain a controlled but vigorous reflux over the course of four hours.
    9. After addition is complete, syringe a small amount of ethyl acetate (2.71 g, 0.0308 mol) into the addition funnel and add dropwise to the reaction over 5 minutes. The mixture will be a cloudy orange/yellow color by the end of these additions. Allow the reaction to stir overnight at ambient temperature.

3. **The next day, replace the addition funnel with a rubber septum.**
    1. Under an argon counter flow, remove the septum and use dry tongs to grab a piece of the unreacted lithium. To recover as much product as possible, rinse the lithium wire quickly with diethyl ether from a wash bottle and allow the solution to drip back into the reaction vessel. Then add the lithium piece to a 500 mL beaker filled with 250 mL of water.
        Caution: The lithium pieces should be added individually to the beaker and the strip should be allowed to fully react before another is added. This minimizes the risk of fire given the significant amount of H_2 generated during the quenching process.
        NOTE: Other methods to quench the excess lithium, such as careful addition to isopropanol, also work but require significantly longer times to fully consume the excess lithium.
    2. Repeat 1.3.1 until all large pieces of lithium are quenched, which should require 60-90 minutes on the given scale.
    3. While still under argon, add a saturated ammonium chloride solution (250 mL) slowly dropwise to the stirring reaction mixture over the course of an hour, quenching the reaction mixture and any small pieces of unreacted lithium. The reaction may reflux gently during the process and become more difficult to stir based on solid formation. Continue addition until the layer of sediment completely dissolves at the bottom of the flask, forming a defined aqueous layer.
    4. Allow the reaction to cool for 30 min after addition of the solution is complete.
    5. Pour the contents of the flask into a 1 L separatory funnel and isolate the diethyl ether layer.
    6. Extract the aqueous layers with three 150 mL portions of diethyl ether.

7. Combine all four diethyl ether layers and rotavap to a volume of approximately 75-100 mL.

2. Synthesis of 1,2,3,4,5-Pentamethylcyclopentadiene (Cp*H)

1. **Attach an oven dried 500 mL three neck round bottom flask, equipped with a reflux condenser and stir bar, to a Schlenk line under a flow of inert gas.**
    1. Charge the flask with *p*-toluene sulfonic acid monohydrate (8.70 g, 0.0457 mol).
    2. Cannula approximately 50 mL of diethyl ether onto the solid.
    3. Under inert gas counter flow, attach an oven dried addition funnel to the reaction setup.
    4. Charge the funnel with the 3,4,5-trimethyl-2,5-heptadien-4-ols/diethyl ether concentrate from Step 1.
    5. Add the concentrate dropwise to the stirring slurry, maintaining a gentle reflux, over the course of 1 h. Allow the reaction to stir for an additional 1 h after the addition is complete.
    6. Pour the reaction mixture into 300 mL of a saturated sodium bicarbonate solution containing 4.59 g (0.0433 mol) of sodium carbonate.
    7. Transfer the contents of the flask into a 1 L separatory funnel and isolate the diethyl ether layer. Extract the aqueous layer with three, 100 mL portions of diethyl ether.
    8. Combine the four diethyl ether layers and dry over magnesium sulfate for two hours.
    9. Filter the mixture and rotavap down the liquid until ~75-100 mL of material remains. At this stage, the concentrate can be stored in a refrigerator overnight prior to purification the following day.

2. **Transfer the concentrate to an oven dried, round bottom flask equipped with a stir bar. Connect this flask to an oven dried transfer manifold equipped with another 100 mL round bottom flask.**
    1. Cool the receiving flask in ice while submerging the concentrate in an ambient temperature water bath.
    2. Apply dynamic vacuum to the setup, while stirring the concentrate, for 30-60 min to remove any residual diethyl ether.
    3. Seal the transfer setup and switch the bath for the receiving flask to a dry ice/acetone slurry while submerging the concentrate in a warm water bath. Allow the trap-to-trap distillation to continue while stirring over the course of 2-3 h, being careful to refresh the vacuum periodically (every 15-20 min) while the baths are also monitored over the same time period.
    NOTE: After transfer, 39.0 g (0.286 moles, 58% based on 2-bromo-2-butene) of Cp*H can be isolated as a pale yellow oil.

3. Synthesis of $[Cp^*RuCl_2]_2$[29]

1. **Charge 1.00 g (3.95 mmol) of ruthenium(III) chloride trihydrate in an oven dried 100 mL Schlenk flask equipped with a stir bar under a flow of inert gas on a Schlenk line.**
    1. Cannula transfer 50 mL of methanol, dried over Mg and distilled prior to use, onto the solid and stir for 30 min.
    2. Filter the solution under inert gas through an oven dried air free filter funnel, filled with an inch of oven dried Celite, into another 100 mL Schlenk flask equipped with a stir bar.
    3. Remove the air-free filter funnel and replace with a septum.
    4. Add Cp*H (1.20 g, 8.81 mmol) by syringe, attach an oven dried reflux condenser equipped with an inert gas sidearm adapter under a flow of inert gas.
    5. Seal the sidearm on the Schlenk flask and reflux for 4 h under a flow of inert gas.

2. **Allow the reaction to cool and replace the reflux condenser with a glass stopper under a flow of inert gas.**
    1. Remove the solvent *in vacuo* and dry on a Schlenk line for three hours. Transfer the flask to a glovebox.
    2. Inside the glovebox, rinse the solid with pentane and scrape the solid from the sides of the flask. Filter the black solid onto a medium porosity frit, rinse with 50 mL of pentane, and dry for an additional hour *in vacuo*.
    Note: $[Cp^*RuCl_2]_2$ (1.53 g, 63% based on Ru) is isolated as a dark solid. Characterization matches literature reports.[29]

4. Synthesis of $[Cp^*IrCl_2]_2$[30]

1. **Charge 1.00 g (2.60 mmol) of iridium(III) chloride hydrate in an oven dried 100 mL Schlenk flask equipped with a stir bar under a flow of inert gas on a Schlenk line.**
    1. Cannula transfer 50 mL of methanol onto the solid.
    2. Add Cp*H (0.50 g, 3.67 mmol) by syringe, attach an oven dried reflux condenser equipped with an inert gas sidearm adapter under a flow of inert gas.
    3. Seal the sidearm on the Schlenk flask and reflux for 48 h under inert gas flow.

2. **Allow the reaction to cool and replace the reflux condenser with a septum under a flow of inert gas.**
    1. Cool the flask in an ice bath for 30 min.
    2. Filter the reaction in air through a 15 mL medium porosity frit.
    3. Rinse with 50 mL of diethyl ether and dry the solid *in vacuo* for two hours.
    NOTE: $[Cp^*IrCl_2]_2$ (1.23 g, 59% based on Ir) is isolated as an orange/red solid. Characterization matches literature reports.[30]

Representative Results

The protocol described above for Cp*H synthesis relies on modification of the three step procedure developed by Bercaw and coworkers and modified by Marks (**Figure 1**). The air sensitive alkenyl lithium is prepared *in situ* from a mixture of *cis* and *trans*-2-butene via a lithium/halogen exchange reaction and is subsequently quenched with ethyl acetate to prepare an isomeric mixture of heptadienols. The mixture can be used without further purification in the acid mediated cyclization to provide the single desired product, Cp*H.

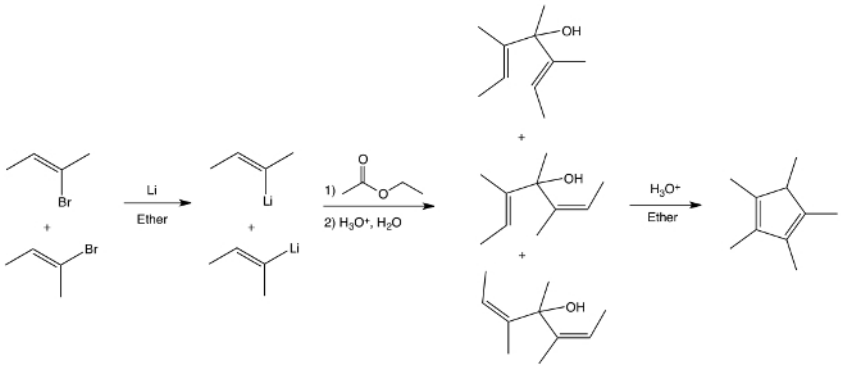

Figure 1: Synthetic scheme for Cp*H synthesis utilized in the described protocol. Please click here to view a larger version of this figure.

With our procedure described above, Cp*H can be consistently isolated in good yields (50-60%) of sufficient purity for subsequent use in direct metallation reactions with mid- to late transition metals or in the preparation of main group pentamethylcyclopentadienide salts.[31] Representative ^{1}H and ^{13}C NMR spectra, recorded in $CDCl_3$, of the Cp*H purified by the trap-to-trap distillation outlined above are provided in **Figure 2**.

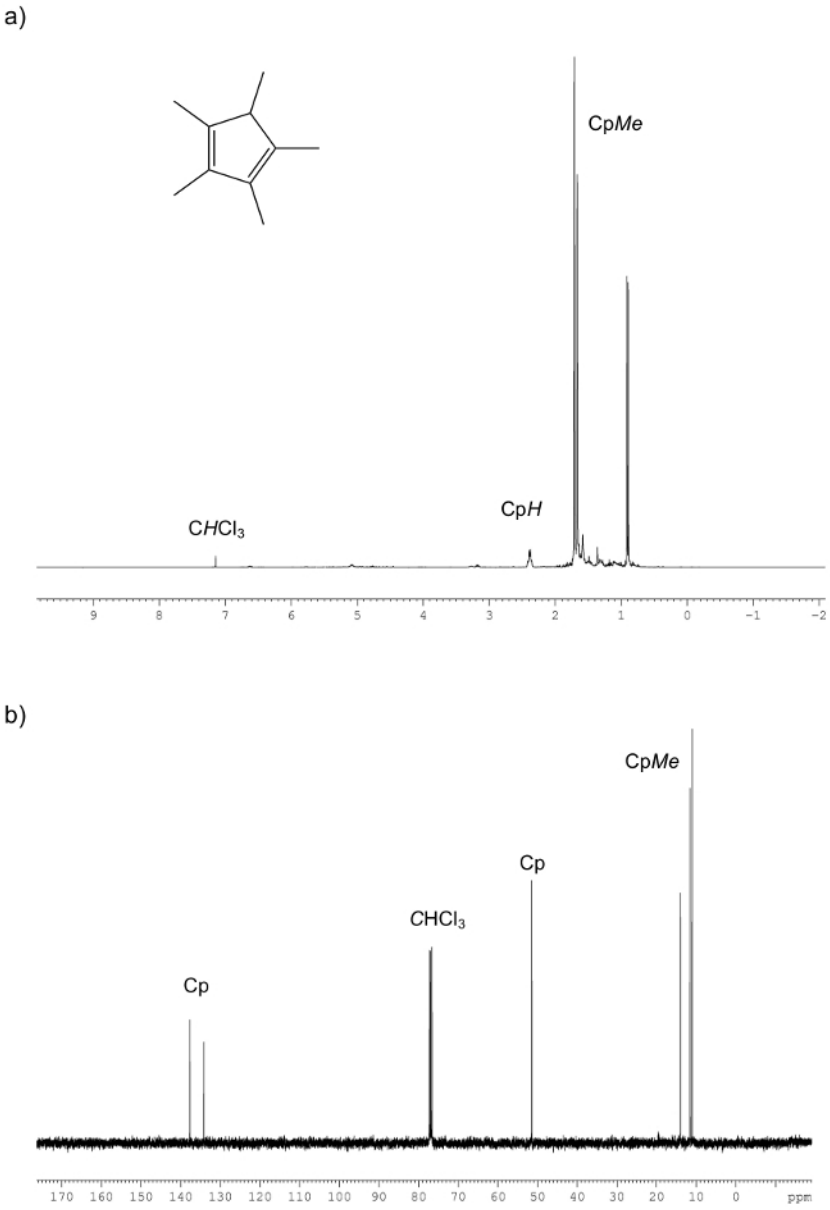

Figure 2: (**a**) ^{1}H NMR spectrum of Cp*H recorded in $CDCl_3$ at 25 °C. (**b**) ^{13}C NMR spectrum of Cp*H recorded in $CDCl_3$ at 25 °C. Please click here to view a larger version of this figure.

To demonstrate the utility of the Cp*H generated by the protocol, two transition metal complexes were prepared using the ligand. The bridging ruthenium(III) halide, $[Cp^*RuCl_2]_2$, is synthesized in moderate yield (63%) by refluxing Cp*H with ruthenium(III) chloride trihydrate in methanol (**Figure 3a**). The air sensitive product was isolated in a glovebox and subsequently characterized under an inert atmosphere. The ^{1}H NMR spectrum of the paramagnetic product matches that of literature reports (**Figure 3b**). The identity of the complex was further confirmed by high-resolution Liquid Injection Field Desorption Ionization (LIFDI)[32] mass spectrometry in chloroform, indicating successful preparation of the desired dimer.

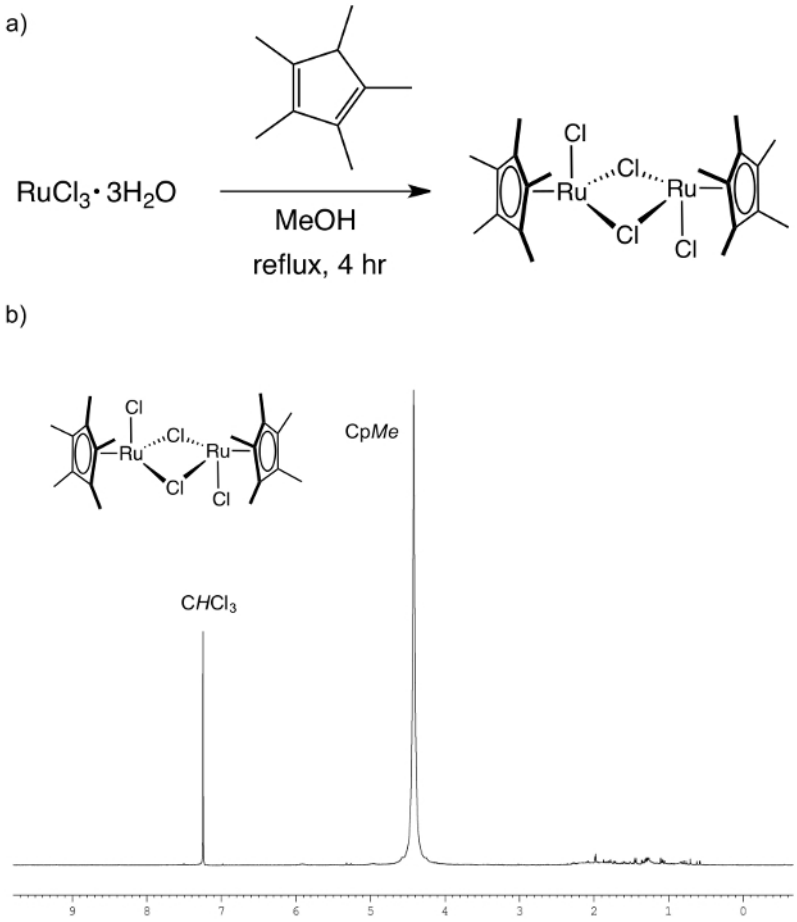

Figure 3: (**a**) Synthesis of $[Cp^*RuCl_2]_2$ utilized in the described protocol. (**b**) ^1H NMR spectrum of $[Cp^*RuCl_2]_2$ recorded in $CDCl_3$ at 25 °C. Please click here to view a larger version of this figure.

The bridging iridium(III) halide, $[Cp^*IrCl_2]_2$, was also prepared in moderate yield (59%) by refluxing Cp*H with iridium(III) chloride hydrate (**Figure 4a**). The air stable product was isolated on the benchtop and subsequently characterized. The ^1H and ^{13}C NMR spectra of the diamagnetic product matches that of prior reports (**Figures 4b** and **4c**). The nuclearity of the complex was further confirmed by high-resolution LIFDI mass spectrometry in chloroform, indicating preparation of the desired dimer.

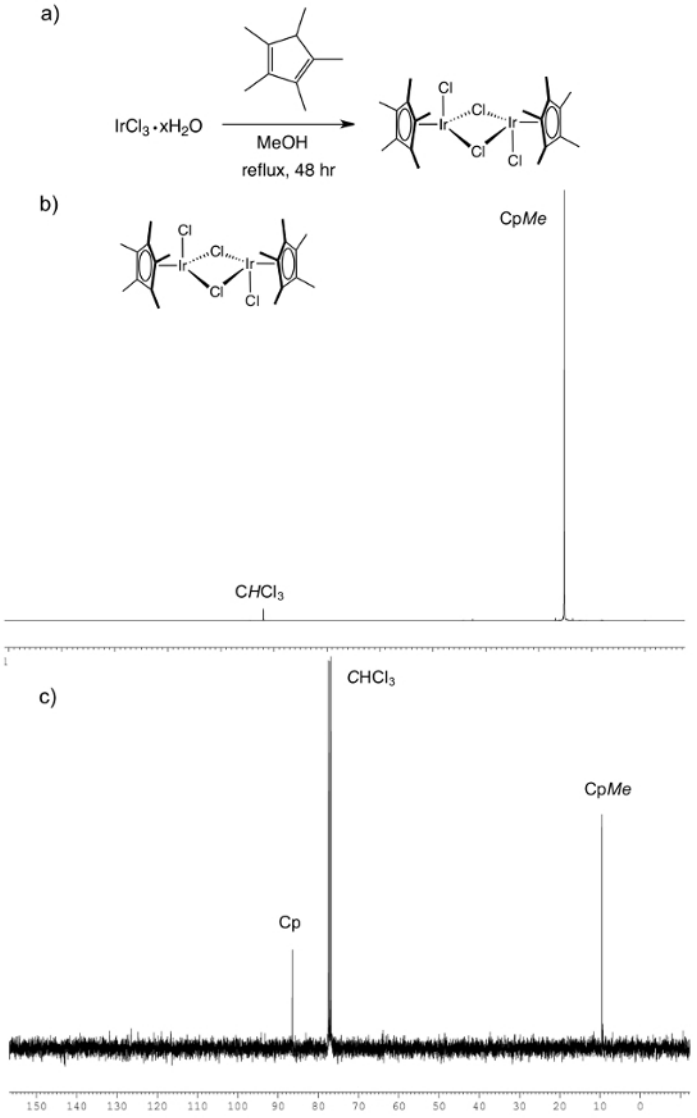

Figure 4: (**a**) Synthesis of $[Cp^*IrCl_2]_2$ utilized in the described protocol. (**b**) ^1H NMR spectrum of $[Cp^*IrCl_2]_2$ recorded in $CDCl_3$ at 25 °C. (**c**) ^{13}C NMR spectrum of $[Cp^*IrCl_2]_2$ recorded in $CDCl_3$ at 25 °C. Please click here to view a larger version of this figure.

Discussion

During preparation of the heptadienol mixture, it is important to clean the lithium prior to initiating the reaction with the 2-bromo-2-butene. This is accomplished by wiping off residual mineral oil used for storage on paper towels, to the point that the oil appears fully removed from the surface, and by dissolving any remaining oil in the beaker of hexanes. The hexanes were used as received and not further dried before use in the procedure. Because of both the large scale of the reaction and an excess of lithium used, the weighing by difference method to determine the lithium mass is adequate. It is important to quench all materials in a hood immediately after cutting and weighing the lithium to minimize the risk of a fire secondary to the reaction vessel, including any residual lithium found on the tongs and scissors. Given the small amount of lithium remaining from the weighing process, we have found it safest to quench quickly with water rather than utilizing other milder routes.

Our group has primarily used lithium purchased commercially (see **Materials**) for the procedure, but similar diameter wire purchased from other vendors still provided isolation of Cp*H in comparable yields. Lithium wire is consistently used because it is simpler to cut into pieces easy to add to the reaction vessel, using only scissors. Regardless of the commercial source of the 2-bromo-2-butene, the lithium/halogen exchange has initiated on its own more than half the time our group has performed the reaction. Use of a heat gun has always provided successful initiation in all other instances. It is *critical* to allow adequate time for the reaction to initiate prior to the addition of large quantities of 2-bromo-2-butene to the mixture to ensure the reaction remains under control. See **Figure 5a** for a representative image of how the reaction mixture looks upon initiation. Isolation of the heptadienols relies on a modified workup procedure, to ensure safer and more controlled lithium quenching. Again, fast reaction of lithium with water has been preferable to other methods, so long as the lithium pieces are allowed to react individually over an adequate period of time. Our research group has never had a fire utilizing this method under controlled conditions. Alternatively, other quenching methods, such as use of isopropanol, work but require significantly longer times for complete consumption of the lithium. This quenching of the excess

lithium outside the reaction vessel makes workup of the reaction much simpler, as all large pieces of Li metal have already been reacted prior to the addition of the ammonium chloride solution. It should be noted that a strong stirrer is recommended for this step (1.3.3), as the reaction mixture can become difficult to stir due to sediment formation until enough of the ammonium chloride solution is added to form a defined aqueous layer. See **Figure 5b** and **5c** for images detailing the typical stages of the reaction quench.

Figure 5: (**a**) Initiation of the lithium halogen exchange with 2-bromo-2-butene. (**b**) Quenching of the heptadienol synthesis after 50 mL of a saturated ammonium chloride solution has been added. (**c**) Quenching of the heptadienol synthesis after 250 mL of a saturated ammonium chloride solution has been added. Please click here to view a larger version of this figure.

During the acid mediated cyclization to form Cp*H (Preparation 2, **Figure 6**), the heptadienols synthesized directly from Preparation 1 or diethyl ether solutions dried using magnesium sulfate prior to performing the reaction have been used, without any impact on the yield of the subsequent reaction. This indicates the exclusion of water in the heptadienol mixture is unnecessary for the cyclization step. Furthermore, the outlined purification (**Figure 6b**) for the Cp*H avoids a fractional distillation. However, the crude material remaining from the trap-to-trap distillation can be combined with material preserved from other Cp*H syntheses and fractionally distilled to provide additional purified ligand.

a)

b)

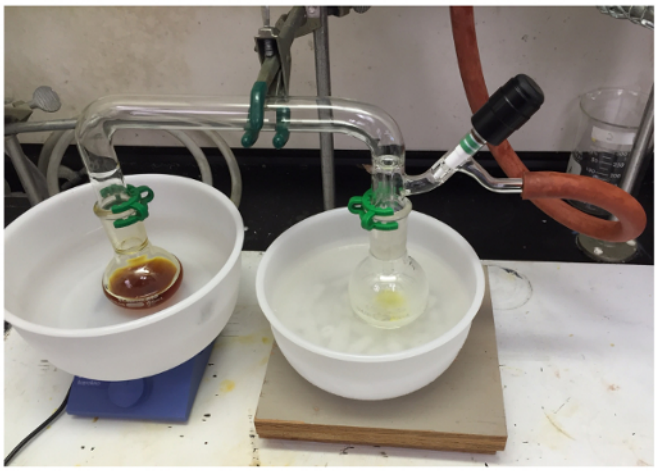

Figure 6: (**a**) Initial reaction setup for dienol cyclization to form Cp*H. (**b**) Trap-to-trap distillation setup for Cp*H purification. Please click here to view a larger version of this figure.

Preparation of Cp*H with this method is usually performed over the course of four days, with the second and third days being the most intensive. The first day involves diethyl ether collection from a solvent purification system as well as drying of the 2-bromo-2-butene and ethyl acetate starting materials. Day 2 involves generation of the butenyl lithium and subsequent reaction with ethyl acetate to prepare the heptadienols. Day 3 encompasses the heptadienol reaction workup along with the acid mediated cyclization. The final day involves purification of Cp*H by the trap-to-trap distillation.

Synthesis of the $[Cp^*MCl_2]_2$ complexes (**Figure 7**) described above demonstrate facile access to transition metal complexes using the Cp*H ligand from our protocol in moderate to good yields. Spectral data on the compounds match literature reports and demonstrate our procedure provides Cp*H of adequate purity for subsequent metallations. Though these reactions were performed on an intermediate scale, synthesis of these complexes should be amenable to larger scale preparation as necessary.

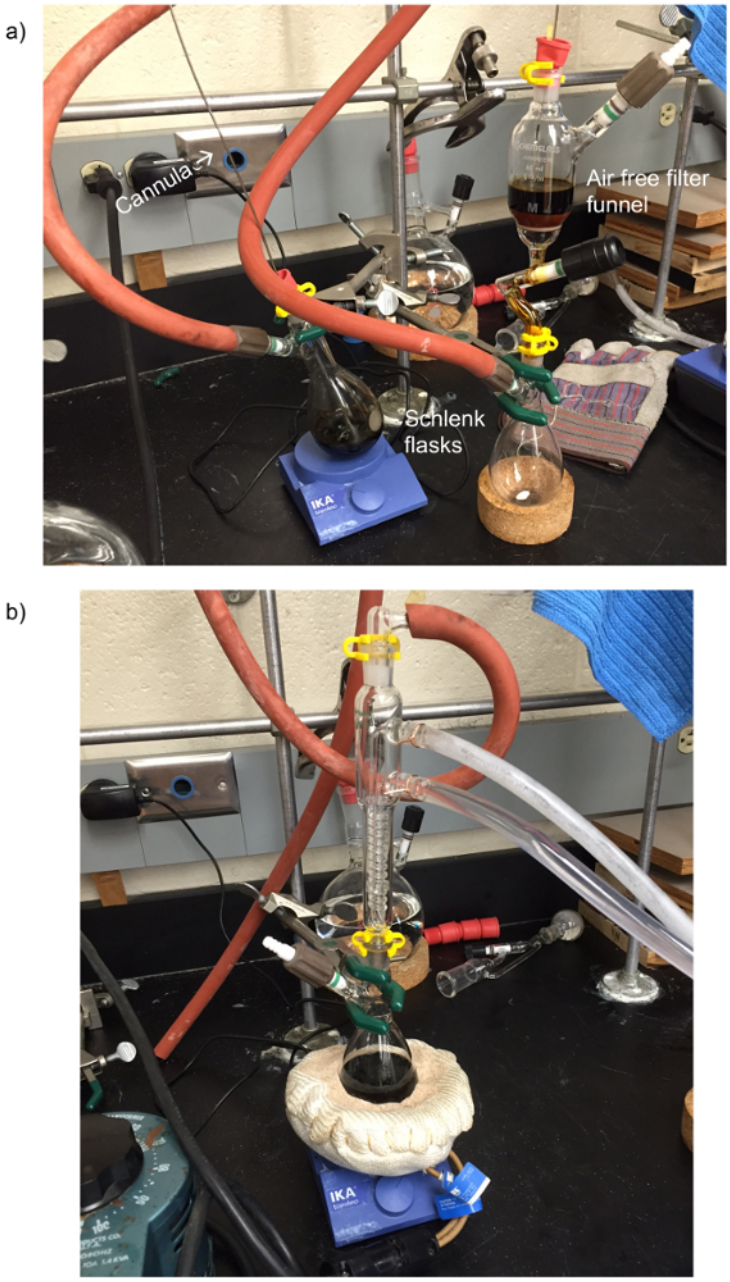

Figure 7: (**a**) Filter assembly setup for isolation of a $RuCl_3$ solution (Step 3.1.2). (**b**) Initial reaction setup for preparation of $[Cp^*RuCl_2]_2$ (Step 3.1.5). Please click here to view a larger version of this figure.

A revised procedure is presented here for access to Cp*H on an intermediate scale which simplifies reaction workups and quenching of excess lithium while providing a streamlined purification for immediate use of the ligand in the preparation of transition metal Cp* complexes. The yields of all reactions are comparable to known literature procedures. This protocol demonstrates value to researchers requiring access to Cp*H on sizable quantities who wish to avoid the use of specialized glassware or laboratory equipment, providing a modified entry point into the chemistry of pentamethylcyclopentadienide metal complexes.

Disclosures

The authors have nothing to disclose.

Acknowledgements

We are grateful to the National Science Foundation (CHE-1300508) and Mount St. Mary's University (Startup and Summer Faculty Development) for generous support of this work. Ben Rupert (University of Delaware, Mass Spectrometry Facility) is acknowledged for LIFDI mass spectral analyses.

References

1. Kealy, T. J., & Pauson, P. L. A new type of organo-iron compound. *Nature.* **168**,1039-1040 (1951).
2. Wilkinson, G., Rosenblum, M., Whiting, M. C., & Woodward, R. B. The structure of iron bis-cyclopentadienyl. *J. Am. Chem. Soc.* **74**, 2125-2126 (1952).
3. Fischer, E. O., & Pfab, W. *Z.* Cyclopentadien-Metallkomplexe, ein neuer Typ metallorganischer Verbindungen. *Z. Naturforsch.* **76**, 377-379 (1952).
4. Pauson, P. L. Ferrocene-how it all began. *J. Organomet. Chem.* **637-639**, 3-6 (2001).
5. Lauher, J. W., & Hoffmann, R. Structure and chemistry of bis(cyclopentadienyl)-ML_n complexes. *J. Am. Chem. Soc.* **98**, 1729-1742 (1976).
6. Resa, I., Carmona, E., Gutierrez-Puebla, E., & Monge, A. Decamethyldizincocene, a stable compound of Zn(I) with a Zn-Zn bond. *Science.* **305**, 1136-1138 (2004).
7. Brintzinger, H., & Bercaw, J. E. Nature of so-called titanocene, $(C_{10}H_{10}Ti)_2$. *J. Am. Chem. Soc.* **92**, 6182-6185 (1970).
8. King, R. B. Some applications of metal carbonyl anions in the synthesis of unusual organometallic compounds. *Acc. Chem. Res.* **3**, 417-427 (1970).
9. Chirik, P. J. Group 4 transition metal sandwich complexes: still fresh after almost 60 years. *Organometallics.* **29**, 1500-1517 (2010).
10. Bengali, A. A., Schultz, R. H., Moore, C. B., & Bergman, R. G. Activation of the C-H bonds in neopentane and neopentane-d_{12} by (η^5-$C_5(CH_3)_5$)$Rh(CO)_2$: Spectroscopic and temporal resolution of rhodium-krypton and rhodium-alkane complex intermediates. *J. Am. Chem. Soc.* **116**, 9585-9589 (1994).
11. Shima, T., Hu, S., Luo, G., Kang, X., Luo, Y., & Hou, Z. Dinitrogen cleavage and hydrogenation by a trinuclear titanium polyhydride complex. *Science.* **340**, 1549-1552 (2013).
12. Negishi, E.-I., & Takahashi, T. Alkene and alkyne complexes of zirconocene. Their preparation, structure, and novel transformations. *Bull. Chem. Soc. Jpn.* **71**, 755-769 (1998).
13. Rosenthal, U., Burlakov, V. V., Arndt, P., Baumann, W., & Spannenberg, A. The titancocene complex of bis(trimethylsilyl)acetylene: Synthesis, structure, and chemistry. *Organometallics* . **22**, 884-900 (2003).
14. Jordan, R. F, Bradley, P. K., LaPointe, R. E, Taylor, D. F. Cationic zirconium catalysts for carbon-carbon bond forming chemistry. *New J. Chem.* **14**, 505-511 (1990).
15. Ewen, J. A. Symmetry rules and reaction mechanisms of Ziegler-Natta catalysts. *J. Mol. Catal.* A **128**, 103-109 (1998).
16. Manriquez, J. M., & Bercaw, J. E. Preparation of a dinitrogen complex of bis(pentamethylcyclopentadienyl)zirconium(II). Isolation and protonation leading to the stoichiometric reduction of dinitrogen to hydrazine. *J. Am. Chem. Soc.* **96**, 6229-6230 (1974).
17. Brintzinger, H. H., Bercaw, J. E. Bis(pentamethylcyclopentadienyl)titanium(II). Isolation and reactions with hydrogen, nitrogen, and carbon monoxide. *J. Am. Chem. Soc.* **93**, 2045-2046 (1971).
18. Lehman, M. C., Gary, J. B., Boyle, P. D, Sanford, M. S., & Ison, E. A. Effect of solvent and ancillary ligands on the catalytic H/D exchange reactivity of $Cp^*Ir^{III}(L)$ complexes. *ACS Catal.* **3**, 2304-2310 (2013).
19. Pitman, C. L., Finster, O. N. L., & Miller, A. J. M. Cyclopentadiene-mediated hydride transfer from rhodium complexes. *Chem. Commun.* **52**, 9105-9108 (2016).
20. Tarantino, K. T., Miller, D. C., Callon, T. A., & Knowles, R. R. Bond-weakening catalysis: Conjugate aminations enabled by the soft homolysis of strong N-H bonds. *J. Am. Chem. Soc.* **137**, 6440-6443 (2015).
21. Bolig, A. D., & Brookhart, M. Activation of sp^3 C-H bonds with cobalt(I): Catalytic synthesis of enamines. *J. Am. Chem. Soc.* **129**, 14544-14545 (2007).
22. Hung-Low, F., Tye, J. W., Cheng, S., & Bradley, C. A. sp^2 C-H activation of dimethyl fumarate by a [$(Cp^*Co)_2$-μ-(η^4:η^4-toluene)] complex. *Dalton Trans.* **41**, 8190-8197 (2012).
23. Hung-Low, F., Krogman, J. P., Tye, J. W., & Bradley, C. A. Development of more labile low electron count Co(I) sources: mild, catalytic functionalization of activated alkanes using a [$(Cp^*Co)_2$-μ-(η^4:η^4-arene)] complex. *Chem. Commun.* **48**, 368-370 (2012).
24. Andjaba, J. M., Tye, J. W., Yu, P., Pappas, I., & Bradley, C. A. Cp*Co(IPr): synthesis and reactivity of an unsaturated Co(I) complex. *Chem. Commun.* **52**, 2469-2472 (2016).
25. Fendrick, C. M., Schertz, L. D., Mintz, E. A., Marks, T. J. Large-scale synthesis of 1,2,3,4,5-pentamethylcyclpentadiene. *Inorg. Synth.* **29**, 193-198 (1992).
26. Threlkel, R. S., & Bercaw, J. E. A Convenient synthesis of alkyltetramethylcyclopentadienes and phenyltetramethylcyclopentadiene. *J. Organomet. Chem.* **136**, 1-5 (1977).
27. Manriquez, J. M., Fagan, P. J., Schertz, L. D, & Marks, T. J. 1,2,3,4,5-pentamethylcyclopentadiene. *Inorg. Synth.* **28**, 317-320 (1990).
28. Threlkel, R. S., Bercaw, J. E., Seidler, P. F., Stryker, J. M., & Bergman, R. G. 1,2,3,4,5-pentamethylcyclopentadiene. *Org. Synth.* **65**, 42 (1987).
29. Koelle, U., & Kossakowski, J. Di-μ-chloro-bis[(η^5-pentachlororuthenium(III)], $[Cp^*RuCl_2]_2$ and Di-μ-methoxo-bis(η^5-pentamethylcyclomethylcyclopentadienyl) diruthenium(II), $[Cp^*RuOMe]_2$. *Inorg. Synth.* **29**, 225-228 (1992).
30. White, C., Yates, A., & Maitlis, P. M. (η^5-pentamethylcyclopentadienyl)rhodium and -iridium compounds. *Inorg. Synth.* **29**, 228-234 (1992).
31. Andersen, R. A., Blom, R., Boncella, J. M, Burns, C. J., & Volden, H. V. The thermal average molecular structures of bis(pentamethylcyclopentadienyl)magnesium(II), -calcium(II), and -ytterbium(II) in the gas phase. *Acta Chem. Scand.* **A41**, 24-35 (1987).
32. Gross, J. H., et al. Liquid injection field desorption/ionization of reactive transition metal complexes. *Anal. Bioanal. Chem.* **386**, 52-58 (2006).

