# METHODS OF MAKING ALKYLATED METALLOCENES HAVING ONE OR MORE TETRAHYDROPENTALENYL GROUPS

## Field of Disclosure

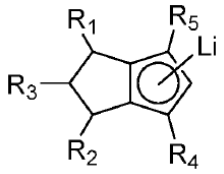
[0001] Embodiments of the present disclosure are directed towards methods of making metallocenes, more specifically, making alkylated metallocenes having one or more tetrahydropentalenyl groups.

## Background

[0002] Metallocenes can be used in various applications, including as polymerization catalysts, as antiknock additives in gasoline, and as lubricants, as well as potential use in medical applications such as cancer, malaria and bacterial infection treatments.

## Summary

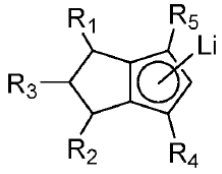
[0003] The present disclosure provides various embodiments, including: a method of making an alkylated metallocene having one or more tetrahydropentalenyl groups, the method comprising: reacting a chloride compound with a lithium compound to make a reaction mixture comprising an intermediate dichloride compound; and reacting the intermediate dichloride compound with an alkylating agent to make the alkylated metallocene having one or more tetrahydropentalenyl groups, wherein the dichloride compound is not isolated from the reaction mixture, wherein the lithium compound is represented by:




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wherein $R_1$, $R_2$, $R_3$, $R_4$, and $R_5$ are each independently H or a (C1-C4) alkyl.

[0003a] In one aspect, the present disclosure provides a method of making an alkylated metallocene having one or more tetrahydropentalenyl groups, the method comprising: reacting a chloride compound with a lithium compound to make a reaction mixture comprising an intermediate dichloride compound; and reacting the intermediate dichloride compound with an alkylating agent to make the alkylated metallocene having one or more tetrahydropentalenyl groups, wherein the dichloride compound is not isolated from the reaction mixture, wherein the lithium compound is represented by:



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wherein $R_1$, $R_2$, $R_3$, $R_4$, and $R_5$ are each independently H or a (C1-C4) alkyl, and wherein the reactions occur in a same reaction vessel.

## Detailed Description

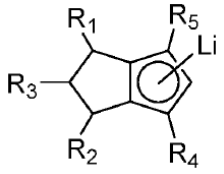
[0004] Previously, alkylated metallocenes have been made by reacting a chloride compound, which contains a metal atom, with a lithium compound to form an intermediate compound that includes the metal atom and a number of chlorine atoms. The reaction forming the intermediate compound can be referred to as a metalation reaction. Following the metalation reaction, the intermediate compound is generally isolated from a reaction mixture that contains unused reactants, byproducts, and/or side-

What is claimed is:

1. A method of making an alkylated metallocene having one or more tetrahydropentalenyl groups, the method comprising:

reacting a chloride compound with a lithium compound to make a reaction mixture comprising an intermediate dichloride compound; and

reacting the intermediate dichloride compound with an alkylating agent to make the alkylated metallocene having one or more tetrahydropentalenyl groups, wherein the dichloride compound is not isolated from the reaction mixture, wherein the lithium compound is represented by:




,

wherein $R_1$, $R_2$, $R_3$, $R_4$, and $R_5$ are each independently H or a (C1-C4) alkyl, and wherein the reactions occur in a same reaction vessel.

2. The method of claim 1, wherein reacting the chloride compound with the lithium compound to make the reaction mixture comprising the intermediate dichloride compound occurs in absence of the alkylating agent.

3. The method of claim 1, wherein the chloride compound includes 3 or 4 chlorine atoms.

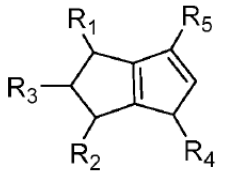
4. The method of claim 1, wherein the chloride compound is selected from zirconium (IV) chloride and n-(propylcyclopentadienyl)hafniumtrichloride (dimethoxyethane).

5. The method of claim 1, wherein the intermediate dichloride compound includes one or more tetrahydropentalenyl groups

6. The method of claim 1, wherein the alkylating agent is an alkylmagnesium halide.

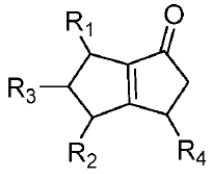
7. The method of claim 1, wherein

the lithium compound is made by reacting butyl lithium with a bicyclic alkene compound represented by:



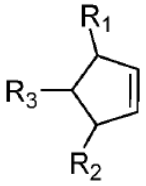

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8. The method of claim 7, wherein the bicyclic alkene compound is made by reacting a bicyclic ketone compound with an alkylating agent and diethyl ether to form a bicyclic alcohol compound and dehydrating the bicyclic alcohol compound to make the bicyclic alkene compound, wherein the bicyclic ketone compound is represented by:

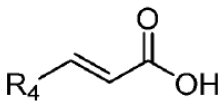



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9. The method of claim 8, wherein the bicyclic ketone compound is made by reacting a cyclic alkene compound represented by:




with an acid compound represented by:




in the presence of a polar aprotic or dipolar aprotic solvent and an effective amount of a phosphoric and/or sulfonic acid reagent and under reaction conditions sufficient to make the bicyclic ketone compound.

10. The method of claim 9, wherein the solvent has a relative polarity above 0.099 and below 0.444, with the proviso that the solvent is not a cyclic ether.

11. The method of claim 9, wherein the phosphoric and/or sulfonic acid reagent is a $P_2O_5/H_3CSO_3H$ mixture.