BICYCLIC HAFNIUM METALLOCENES HAVING NONIDENTICAL LIGANDS

Field of Disclosure

[0001] Embodiments of the present disclosure are directed towards bicyclic hafnium metallocenes having nonidentical ligands and compositions including bicyclic hafnium metallocenes having nonidentical ligands.

Background

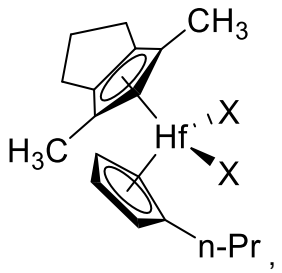
[0002] Metallocenes can be used in various applications, including as polymerization catalysts. Polymers may be utilized for a number of products including films, among others. Polymers can be formed by reacting one or more types of monomer in a polymerization reaction. There is continued focus in the industry on developing new and improved materials and/or processes that may be utilized to form polymers.

Summary

[0003] The present disclosure provides various examples, including:

[0004] A bicyclic hafnium metallocene having nonidentical ligands represented by formula (I): $ABMX_2$, where: A is a bicyclic structure; and B is a cyclopentadienyl; M is hafnium; and X is a leaving group, wherein the bicyclic structure comprises a $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring and a non-aromatic cyclic structure fused with the $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring such that the bicyclic structure includes 7 to 9 ring carbon atoms and wherein subscript n is 1, 2, or 3.

[0004a] In one aspect, the present disclosure provides a bicyclic hafnium metallocene having nonidentical ligands represented by formula (I): $ABMX_2$, where: A is a bicyclic structure; and B is a cyclopentadienyl; M is hafnium; and X is a leaving group, wherein the bicyclic structure comprises a $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring and a non-aromatic cyclic structure fused with the $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring such that the bicyclic structure includes 7 to 9 ring carbon atoms and wherein subscript n is 1, 2, or 3, wherein the bicyclic hafnium metallocene having nonidentical ligands is represented by structure (II):



wherein X is Cl or Me.

[0004b] A bicyclic hafnium metallocene catalyst composition comprising: a bicyclic hafnium metallocene having nonidentical ligands represented by formula (I): $ABMX_2$, where: A is a bicyclic structure; and B is a cyclopentadienyl; M is hafnium; and X is a leaving group, wherein the bicyclic structure comprises a $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring and a non-aromatic cyclic structure fused with the $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring such that the bicyclic structure includes 7 to 9 ring carbon atoms and wherein subscript n is 1, 2, or 3; and an activator.

[0004c] In another aspect, the present disclosure provides a bicyclic hafnium metallocene catalyst composition comprising: a bicyclic hafnium metallocene as defined herein; and an activator

[0005] A method of making a polymer, the method comprising: contacting the bicyclic hafnium metallocene catalyst composition comprising: a bicyclic hafnium metallocene having nonidentical ligands represented by formula (I): $ABMX_2$, where: A is a bicyclic structure; and B is a cyclopentadienyl; M is hafnium; and X is a leaving group, wherein the bicyclic structure comprises a $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl

ring and a non-aromatic cyclic structure fused with the $((C_1\text{-}C_6)\text{alkyl})_n$-substituted cyclopentadienyl ring such that the bicyclic structure includes 7 to 9 ring carbon atoms and wherein subscript n is 1, 2, or 3; and an activator, with an olefin under polymerization conditions to make the polymer.

[0005a] In another aspect, the present disclosure provides a method of making a polymer, the method comprising: contacting the bicyclic hafnium metallocene catalyst composition as defined herein, with an olefin under polymerization conditions to make the polymer.

Brief Description of the Drawings

[0006] Figure 1 shows molecular weight comonomer distribution index (MWCDI) in accordance a number of embodiments of the present disclosure.

Detailed Description

[0007] Bicyclic hafnium metallocenes having nonidentical ligands are discussed herein. Advantageously, these bicyclic hafnium metallocenes having nonidentical ligands can be utilized to make catalyst compositions, for instance. These catalyst compositions can be utilized to make polymers having an improved, i.e. greater, molecular weight comonomer distribution index (MWCDI) as compared to polymers having a similar density, e.g. $\pm$ 0.0025 g/cm^3, made from other hafnium metallocenes. These polymers are desirable for a number of applications, including films, among others. As such, providing an improved MWCDI is advantageous. Further, the compositions disclosed herein can be utilized to make polymers desirably having an improved, e.g. greater, weight average molecular weight (M_w) to number average molecular weight (M_n) ratio (Mw/Mn), and/or an improved, e.g., reduced, melt index (I_{21}), as compared to polymers made from other hafnium metallocenes. Such polymers are advantageous for a number of applications.

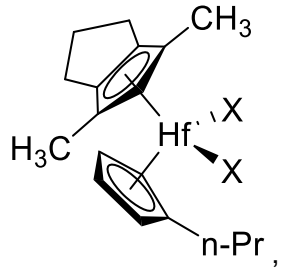
[0008] The bicyclic hafnium metallocenes having nonidentical ligands disclosed herein, can be represented by formula (I): $ABMX_2$, where: A is a bicyclic structure; and B is a substituted cyclopentadienyl; M is hafnium; and X is a leaving group, wherein the bicyclic structure comprises a $((C_1\text{-}C_6)\text{alkyl})_n$-substituted cyclopentadienyl ring and a non-aromatic cyclic structure fused with the $((C_1\text{-}C_6)\text{alkyl})_n$-substituted cyclopentadienyl ring such that the bicyclic structure includes 7 to 9 ring carbon atoms and wherein subscript n is 1, 2, or 3. Because embodiments of the present disclosure provide that A

is different than B, the hafnium metallocenes are referred to as having nonidentical ligands.

[0009] For the formula $ABMX_2$, where A is a bicyclic structure, A includes two cyclic structures, i.e. a cyclopentadienyl ring and non-aromatic cyclic structure fused together. One or more embodiments provide that the A bicyclic structure is a

What is claimed is:

1. A bicyclic hafnium metallocene having nonidentical ligands represented by formula (I): $ABMX_2$, where: A is a bicyclic structure; and B is a cyclopentadienyl; M is hafnium; and X is a leaving group, wherein the bicyclic structure comprises a $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring and a non-aromatic cyclic structure fused with the $((C_1\text{-}C_6)alkyl)_n$-substituted cyclopentadienyl ring such that the bicyclic structure includes 7 to 9 ring carbon atoms and wherein subscript n is 1, 2, or 3, wherein the bicyclic hafnium metallocene having nonidentical ligands is represented by structure (II):



wherein X is Cl or Me.

2. A bicyclic hafnium metallocene catalyst composition comprising:
a bicyclic hafnium metallocene according to claim 1; and
an activator.

3. The bicyclic hafnium metallocene catalyst composition of claim 2 further comprising a support.

4. The bicyclic hafnium metallocene catalyst composition of claim 2 or 3, wherein a molar ratio of metal in the activator to hafnium in the bicyclic hafnium metallocene having nonidentical ligands is 1500: 1 to 0.5: 1.

5. The bicyclic hafnium metallocene catalyst composition of any one of claims 2 to 4, wherein the composition is spray-dried.

6. A method of making a polymer, the method comprising:
contacting the bicyclic hafnium metallocene catalyst composition according to claim 2,

with an olefin under polymerization conditions to make the polymer.

7. The method of claim 6, wherein the polymer has a molecular weight comonomer distribution index (MWCDI) from 0.08 to 2.50.

8. The method of claim 6 or 7, wherein the bicyclic hafnium metallocene catalyst composition is supported.

9. The method of any one of claims 6 to 8, wherein the bicyclic hafnium metallocene catalyst composition is spray-dried.

10. The method of any one of claims 6 to 9, wherein contacting the bicyclic hafnium metallocene catalyst composition and the olefin under polymerization conditions to make the polymer occurs in a gas-phase polymerization reactor.