METAL COMPLEXES

Field of Disclosure

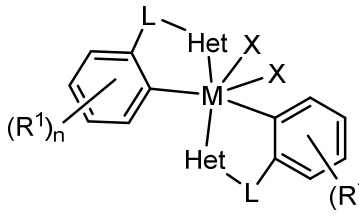
[0001] Embodiments of the present disclosure are directed towards metal complexes, more specifically, embodiments are directed towards metal complexes that can be utilized to form polymers.

Background

[0002] Polymers may be utilized for a number of products including films and pipes, among other. 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

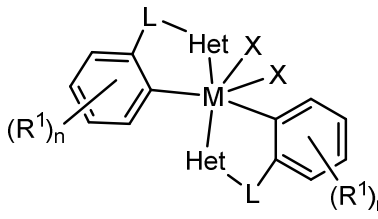
[0003] The present disclosure provides metal complexes of Formula I:



Formula I

[0004] wherein M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

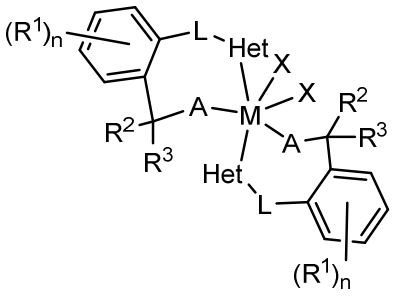
[0004a] In one aspect the present disclosure refers to a metal complex of Formula I:



Formula I

wherein M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

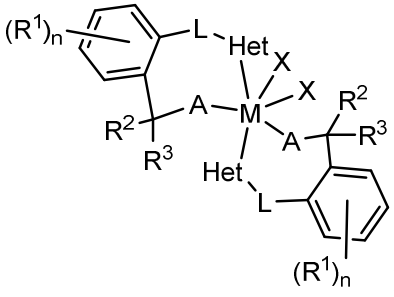
[0005] The present disclosure provides metal complexes of Formula II:



Formula II

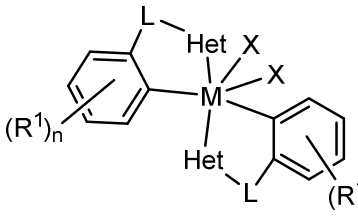
wherein the metal complex of Formula II is formed by reacting a metal complex of Formula I with a polar organic material selected from the group of ketones, aldehydes, imines, and combinations thereof; each A is independently O, S, or N-R^4; and each R^2, R^3 and, R^4 are independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof or R^2 and R^3 are combined to be an oxo group, an alkylimino group, or a thio group.

[0005a] In another aspect, the present disclosure refers to a metal complex of Formula II:



Formula II

wherein the metal complex of Formula II is formed by reacting the metal complex of Formula I



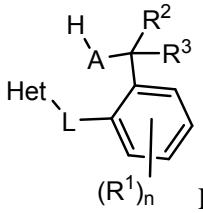
Formula I

with a polar organic material selected from the group of ketones, aldehydes, imines, and combinations thereof;

wherein in Formula II, each A is independently O, S, or N-R^4; and each R^2, R^3 and, R^4 are independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof or R^2 and R^3 are combined to be an oxo group, an alkylimino group, or a thio group; and

wherein in Formula I and Formula II, M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

[0006] The present disclosure provides organic compounds of Formula III:



Formula III

wherein the organic compound of Formula III is formed by reacting a metal complex of Formula II with a protic material ; each A is independently O, S, or N-R^4; and each R^2, R^3 and, R^4 are independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols,

dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof or R^2 and R^3 are combined to be an oxo group, an alkylimino group, or a thio group.

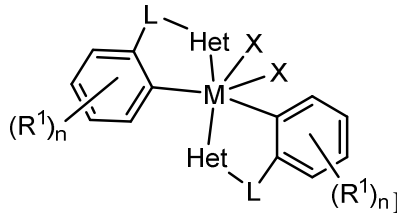
[0007] The present disclosure provides supported metal complexes including the metal complex of Formula I, an activator, and a support materal.

[0008] The present disclosure provides supported metal complexes including the metal complex of Formula II, an activator, and a support materal.

[0009] The present disclosure provides methods for forming a metal complex including reacting an aryl-heteroaryl compound with a metal dihalide precursor to form a metal complex of Formula I.

[0009a] In another aspect, the present disclosure refers to a method for forming a metal complex comprising:

reacting an aryl-heteroaryl compound with a metal dihalide precursor to form a metal complex of Formula I:



Formula I

wherein M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

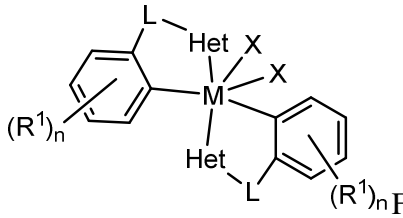
[0010] The methods can include reacting the metal complex of Formula I with a polar organic material selected from the group of and combinations thereof to form a metal complex of Formula II.

[0011] The present disclosure provides methods for forming organic compounds of Formula III.

[0012] The present disclosure provides methods for forming a polymer including contacting an olefin with a metal complex of Formula I.

[0012a] In another aspect, the present disclosure refers to a method of forming a polymer comprising:

contacting an olefin with a metal complex of Formula I:



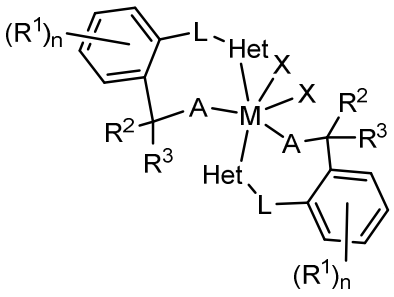
Formula I

wherein M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

[0013] The present disclosure provides methods for forming a polymer including contacting an olefin with a metal complex of Formula II.

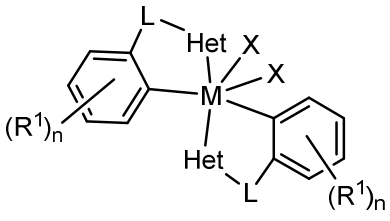
[0013a] In yet another aspect, the present disclosure refers to method of forming a polymer comprising:

contacting an olefin with a metal complex of Formula II:



Formula II

wherein the metal complex of Formula II is formed by reacting the metal complex of Formula I



Formula I

with a polar organic material selected from the group of ketones, aldehydes, imines, and combinations thereof;

wherein in Formula II, each A is independently O, S, or N-R^4; and each R^2, R^3 and, R^4 are independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof or R^2 and R^3 are combined to be an oxo group, an alkylimino group, or a thio group; and

wherein in Formula I and Formula II, M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-

carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

[0014] The above summary of the present disclosure is not intended to describe each disclosed embodiment or every implementation of the present disclosure. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance is provided through lists of examples, which examples can be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

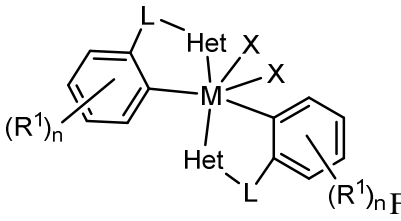
Detailed Description

[0015] Metal complexes and methods of forming the same are described herein. The metal complexes described herein may be utilized as polymerization catalysts. For instance, embodiments of the present disclosure can provide an activity of 1000 grams of polymer per gram of supported metal complex, e.g., a supported catalyst as discussed herein, 1200 grams of polymer per gram of supported metal complex, 1400 grams of polymer per gram of supported metal complex, or even a greater activity. Additionally, unlike previous metal complexes, the metal complexes disclosed herein may advantageously be formed without a ligand purification step. Forming metal complexes without a ligand purification step may reduce manufacturing times and/or manufacturing

Claims

What is claimed:

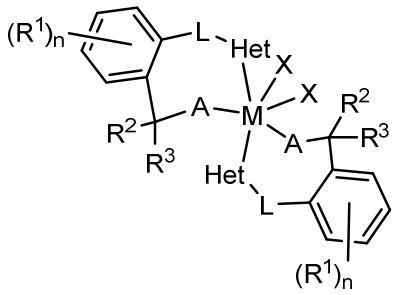
1. A metal complex of Formula I:



Formula I

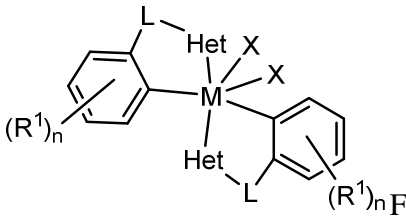
wherein M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

2. A metal complex of Formula II:



Formula II

wherein the metal complex of Formula II is formed by reacting the metal complex of Formula I



Formula I

with a polar organic material selected from the group of ketones, aldehydes, imines, and combinations thereof;

wherein in Formula II, each A is independently O, S, or N-R^4; and each R^2, R^3 and, R^4 are independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof or R^2 and R^3 are combined to be an oxo group, an alkylimino group, or a thio group; and

wherein in Formula I and Formula II, M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

3. The metal complex of claim 2, wherein M is Zr.

4. A supported metal complex comprising:

the metal complex of claim 1;

an activator; and

a support material.

5. A supported metal complex comprising:

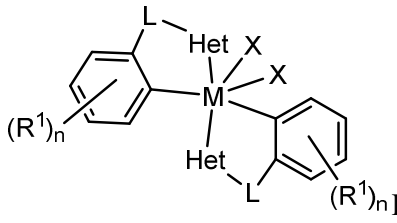
the metal complex of claim 2;

an activator; and

a support material.

6. A method for forming a metal complex comprising:

reacting an aryl-heteroaryl compound with a metal dihalide precursor to form a metal complex of Formula I:



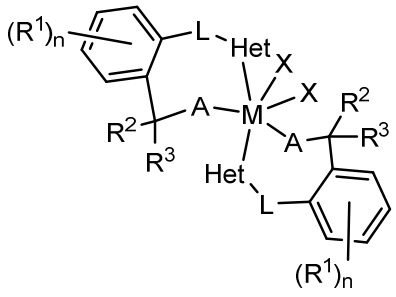
Formula I

wherein M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

7. The method of claim 6, wherein the metal dihalide is dibenzyldichlorozirconium etherate.

8. The method of claim 6, futher comprising:

reacting the metal complex of claim 6 with a polar organic material selected from the group of ketones, aldehydes, imines, and combinations thereof to form a metal complex of Formula II:



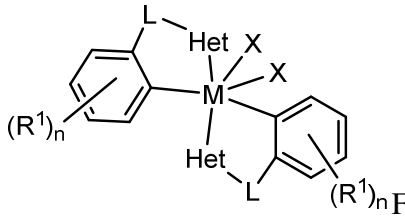
Formula II

wherein each A is independently O, S, or N-R^4; each R^2, R^3 and, R^4 are independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos,

alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof or R^2 and R^3 are combined to be an oxo group, an alkylimino group, or a thio group; M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

9. A method of forming a polymer comprising:

contacting an olefin with a metal complex of Formula I:

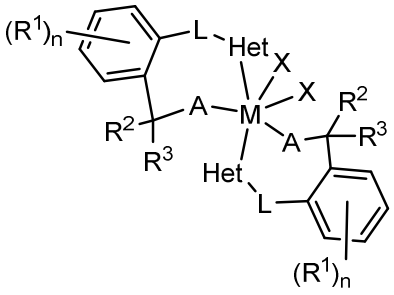


Formula I

wherein M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is

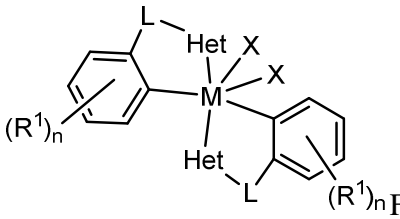
independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.

10. A method of forming a polymer comprising:
contacting an olefin with a metal complex of Formula II:



Formula II

wherein the metal complex of Formula II is formed by reacting the metal complex of Formula I



Formula I

with a polar organic material selected from the group of ketones, aldehydes, imines, and combinations thereof;
wherein in Formula II, each A is independently O, S, or N-R^4; and each R^2, R^3 and, R^4 are independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof or R^2 and R^3 are combined to be an oxo group, an alkylimino group, or a thio group; and

wherein in Formula I and Formula II, M is Zr, Hf, or Ti; each Het is independently a heterocyclic; each L is independently a bridging group $(CR_2)_m$ where m is 0, 1, 2, 3, or 4; O; S; or NR-, where each R is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings and combinations thereof; each X is independently Cl, Br, I, or alkyl; each R^1 is independently selected from the group including hydrogen, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidos, alkoxycarbonyls, aryloxycarbonyls, carbomoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, aroylaminos, aromatic rings, fused aromatic rings, and combinations thereof; and each n is independently an integer having a value of one to five.