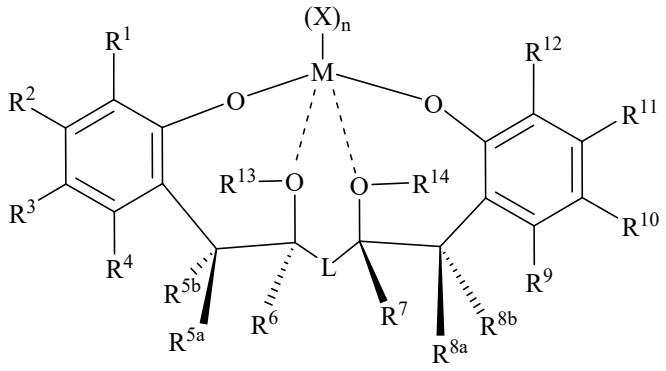
or polypropylene polymerization, there is still a need to increase the efficiencies of catalyst systems that are capable of producing polymer with high molecular weights and a narrow molecular weight distribution.

SUMMARY

[0004] Ongoing needs exist for molecular olefin polymerization catalysts that can polymerize mixtures of ethylene and alpha-olefins that operate at high efficiencies (greater than 1,000,000 gpoly/gM) and temperatures (of greater than or equal to 150 °C).

[0005] This disclosure include one or more catalyst systems. The catalyst systems include one or more metal–ligand complexes according to formula (I):



(I)

[0006] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4; each X is a monodentate or bidentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, $(C_1–C_{50})$hydrocarbyl, cyclopentadienyl, substituted cyclopentadienyl, $(C_4–C_{12})$diene, halogen, and $–CH_2SiR^C_3$; wherein each R^C is selected from the group consisting $(C_1–C_{30})$hydrocarbyl or –H. In formula (I), subscript n of $(X)_n$ is 2. The metal–ligand complex of formula (I) has 6 or fewer metal−ligand bonds.

[0007] In one or more examples, the metal−ligand complex of formula (I) M is zirconium or hafnium; each X is independently chosen from unsubstituted $(C_1–C_{10})$alkyl, substituted $(C_1–C_{10})$alkyl, $(C_6–C_{20})$aryl or a halogen; and each R^1 is independently chosen from $(C_6–C_{50})$aryl or $(C_1–C_{50})$alkyl.

[0008] In examples, the dotted lines are optionally dative bonds between the metal center, M, and the oxygen, O. In some examples, one of the dotted lines connecting O and

M is dative and the other dotted line does not form a dative bond between O and M. In various examples, both dotted lines form dative bonds between group O and M.

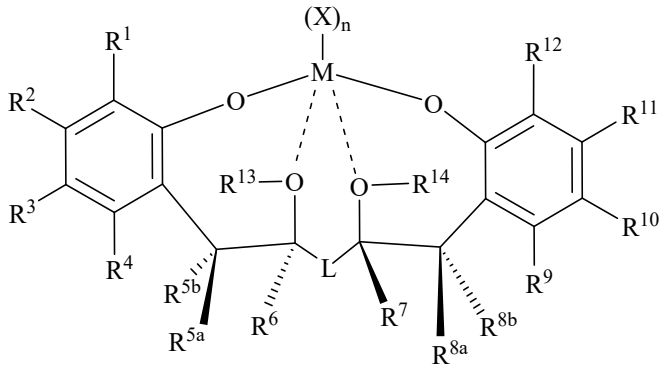
[0009] In formula (I), L is (C_1−C_{10})hydrocarbylene or a bond.

[0010] In formula (I), R^1 R^2, R^3, R^4, R^9, R^{10}, R^{11}, and R^{12} is independently selected from the group consisting of –H, (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, and halogen atom.

[0011] In formula (I), R^{5a} and R^{5b} and R^{8a} and R^{8b} is selected from –H, (C_1−C_{40})hydrocarbyl, (C_6−C_{40})heterohydrocarbyl, and halogen atom. In some examples, R^{5a} and R^{5b} can be linked to form a cyclic structure. In various examples, R^{8a} and R^{8b} can be linked to form a cyclic structure.

[0012] In formula (I), R^6 and R^7 is independently selected from –H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})heterohydrocarbyl, wherein R^6 and R^7 can optionally combine together to form a cyclic structure. R^{13} and R^{14} is independently selected from (C_1−C_{40})hydrocarbyl and (C_1−C_{40})heterohydrocarbyl.

[0012a] In one aspect, there is provided a catalyst system comprising one or more metal−ligand complexes according to formula (I):



(I)

where:

M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

each dotted line represents an optional dative bond between O and M;

each X is a monodentate or bidentate ligand independently chosen from unsaturated (C_2−C_{50})hydrocarbon, unsaturated

(C_2−C_{50})heterohydrocarbon, (C_1−C_{50})hydrocarbyl, cyclopentadienyl, substituted cyclopentadienyl, (C_4−C_{12})diene, halogen;

n is 2;

the metal–ligand complex has 6 or fewer metal−ligand bonds;

L is (C_1−C_{10})hydrocarbylene or a bond;

R^1 R^2, R^3, R^4, R^9, R^{10}, R^{11}, and R^{12} is independently selected from the group consisting of –H, (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, and halogen atom;

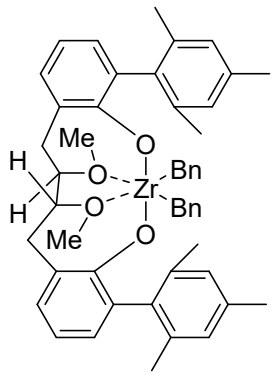
R^{5a} and R^{5b} and R^{8a} and R^{8b} is selected from –H, (C_1−C_{40})hydrocarbyl, (C_6−C_{40})heterohydrocarbyl, and halogen atom, wherein R^{5a} and R^{5b} can optionally combine together to form a cyclic structure, and R^{8a} and R^{8b} can optionally combine together to form a cyclic structure;

R^6 and R^7 is independently selected from –H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})heterohydrocarbyl, wherein R^6 and R^7 can optionally combine together to form a cyclic structure; and

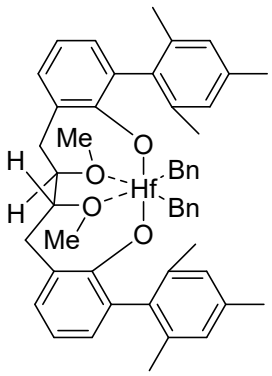
R^{13} and R^{14} is independently selected from (C_1−C_{40})hydrocarbyl and (C_1−C_{40})heterohydrocarbyl.

[0012b] In another aspect, there is provided a polymerization process for polymerizing olefin monomers, the process comprising contacting ethylene and optionally one or more α-olefin monomers in the presence of a catalysts system, the catalyst system as defined herein, in a polymerization reactor at a reactor temperature.

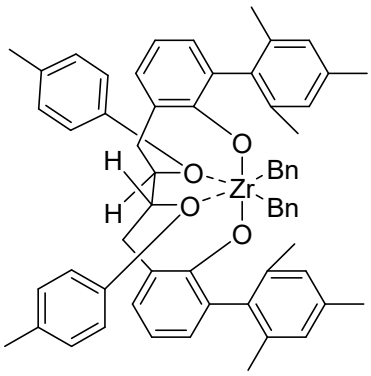
[0012c] In another aspect, there is provided a metal−ligand complex according to any one of the following:



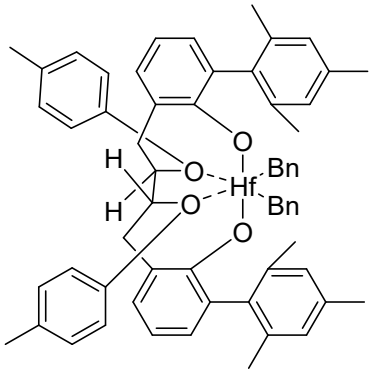
Metal−Ligand Complex 1



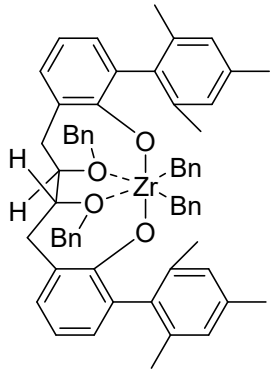
Metal−Ligand Complex 2



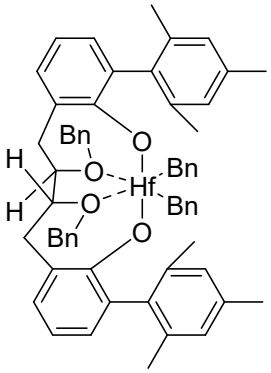
Metal−Ligand Complex 3



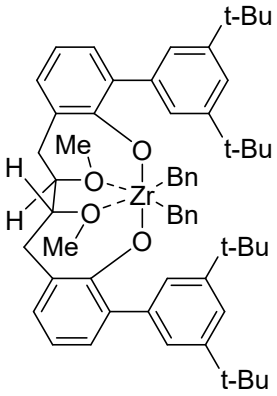
Metal−Ligand Complex 4



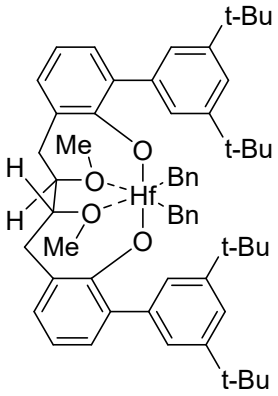
Metal−Ligand Complex 5



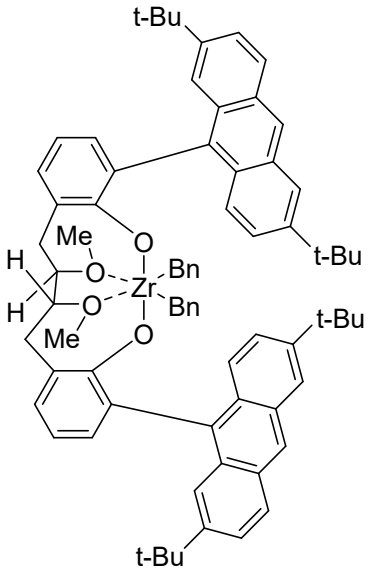
Metal−Ligand Complex 6



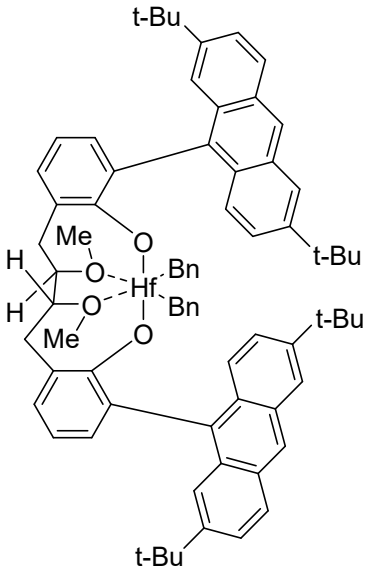
Metal−Ligand Complex 7



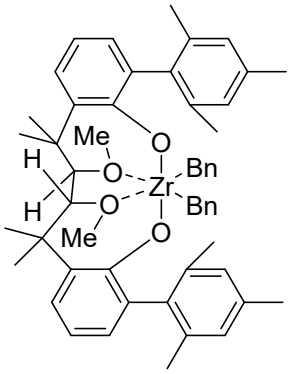
Metal−Ligand Complex 8



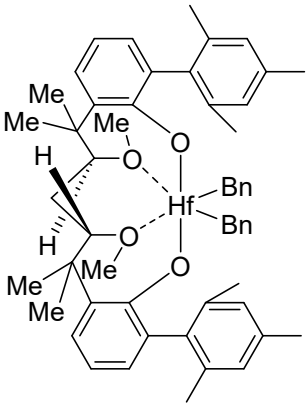
Metal−Ligand Complex 9



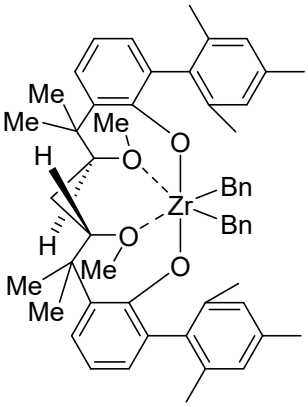
Metal−Ligand Complex 10



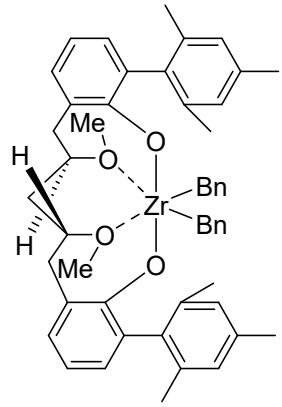
Metal−Ligand Complex 11



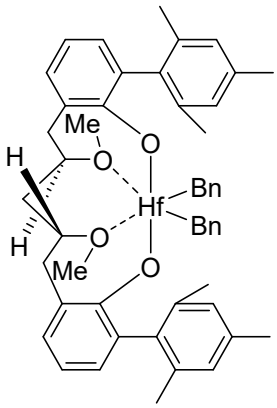
Metal−Ligand Complex 12



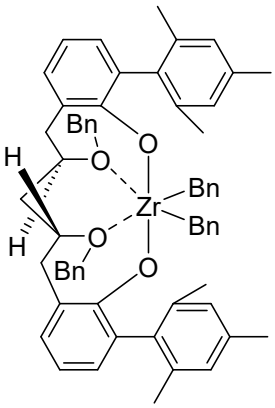
Metal−Ligand Complex 13



Metal−Ligand Complex 14



Metal−Ligand Complex 15



Metal−Ligand Complex 16

DETAILED DESCRIPTION

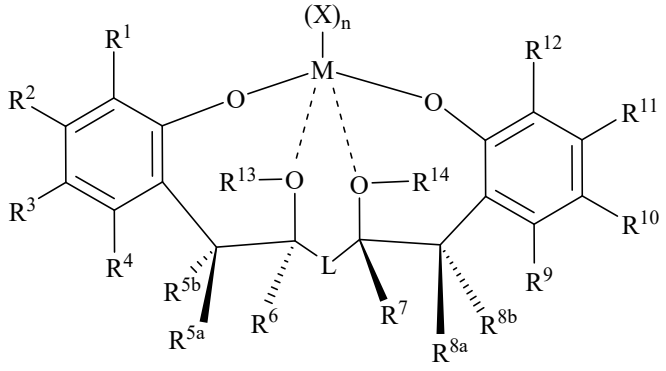
[0013] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure.

[0014] Common abbreviations are listed below:

[0015] **R, Z, M, X and n**: as defined above; **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn**: benzyl; ***i*-Pr** : *iso*-propyl; ***t*-Bu** : *tert*-butyl; ***t*-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf** : trifluoromethane sulfonate; **CV** : column volume (used in column chromatography); **EtOAc** : ethyl acetate; **TEA :** triethylaluminum; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **$LiCH_2TMS$**: (trimethylsilyl)methyllithium; **TMS** : trimethylsilyl; **Pd(AmPhos)Cl_2:** Bis(di-tert-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II); **Pd(AmPhos):** Chloro(crotyl)(di-tert-butyl(4-dimethylaminophenyl)phosphine)palladium(II); **Pd(dppf)Cl_2:** [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride**;** **$ScCl_3$**: scandium(III) chloride; **PhMe**: toluene; **THF**: tetrahydrofuran; **CH_2Cl_2**: dichloromethane;

CLAIMS

1. A catalyst system comprising one or more metal−ligand complexes according to formula (I):



(I)

where:

M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

each dotted line represents an optional dative bond between O and M;

each X is a monodentate or bidentate ligand independently chosen from unsaturated (C_2−C_{50})hydrocarbon, unsaturated (C_2−C_{50})heterohydrocarbon, (C_1−C_{50})hydrocarbyl, cyclopentadienyl, substituted cyclopentadienyl, (C_4−C_{12})diene, halogen;

n is 2;

the metal–ligand complex has 6 or fewer metal−ligand bonds;

L is (C_1−C_{10})hydrocarbylene or a bond;

R^1 R^2, R^3, R^4, R^9, R^{10}, R^{11}, and R^{12} is independently selected from the group consisting of –H, (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, and halogen atom;

R^{5a} and R^{5b} and R^{8a} and R^{8b} is selected from –H, (C_1−C_{40})hydrocarbyl, (C_6−C_{40})heterohydrocarbyl, and halogen atom, wherein R^{5a} and R^{5b} can optionally combine together to form a cyclic structure, and R^{8a} and R^{8b} can optionally combine together to form a cyclic structure;

R^6 and R^7 is independently selected from –H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})heterohydrocarbyl, wherein R^6 and R^7 can optionally combine together to form a cyclic structure; and

R^{13} and R^{14} is independently selected from $(C_1–C_{40})$hydrocarbyl and $(C_1–C_{40})$heterohydrocarbyl.

2. The catalyst system according to claim 1, wherein n is 2 and each X is independently $(C_{1_}C_{12})$alkyl, phenyl, benzyl, or halogen atom.

3. The catalyst system of claim 1 or claim 2, wherein R^{13} and R^{14} is $(C_1–C_{12})$alkyl, substituted phenyl, unsubstituted phenyl, substituted benzyl, or unsubstituted benzyl.

4. The catalyst system of any one of the preceding claims, wherein R^1 and R^{12} a substituted phenyl or unsubstituted phenyl.

5. The catalyst system of any one of the preceding claims, wherein R^1 and R^{12} is 2,4,6-trimethylphenyl or 3,5-di-tert-butylphenyl.

6. The catalyst system of any one of claims 1 to 3, wherein R^1 and R^{12} is a substituted or unsubstituted anthracenyl.

7. The catalyst system of claim 6, wherein R^1 and R^{12} is di-*tert*-butylanthracenyl.

8. The catalyst system of any one of the preceding claims, wherein R^{5a}, R^{5b}, R^{8a}, and R^{8b} is –H.

9. The catalyst system of any one of claims 1 to 7, wherein R^{5a}, R^{5b}, R^{8a}, and R^{8b} is $(C_1–C_{12})$alkyl.

10. The catalyst system of any one of claims 1 to 7, wherein one of R^{5a} and R^{5b} is methyl and one of R^{8a} and R^{8b} is methyl.

11. The catalyst system of any one of the preceding claims, wherein R^3 and R^{10} a substituted phenyl or unsubstituted phenyl.

12. The catalyst system of any one of the preceding claims, wherein L is $(C_1–C_{10})$alkylene.

13. The catalyst system of claim 12, wherein L is selected from the group consisting of methylene, ethylene, and 1,3-propylene.

14. The catalyst system of any one of the preceding claims, wherein the catalyst system further comprises an activator.

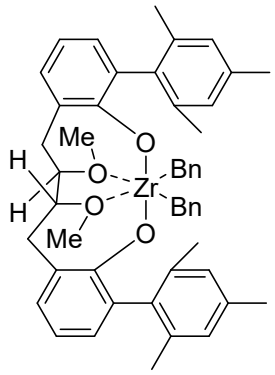
15. A polymerization process for polymerizing olefin monomers, the process comprising contacting ethylene and optionally one or more α-olefin monomers in the presence of a catalysts system, the catalyst system according to any one of claims 1 to 8, in a polymerization reactor at a reactor temperature.

16. The polymerization process of claim 15, wherein the reactor temperature is greater than 100 °C and less than 300 °C.

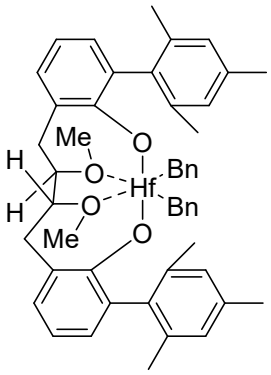
17. The polymerization process of claim 15 or claim 16, wherein the polymerization reactor is a solution reactor.

18. The polymerization process of any one of claims 15 to 17, wherein the process further comprises a solvent.

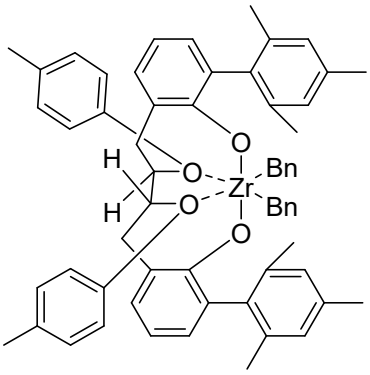
19. A metal−ligand complex according to any one of the following:



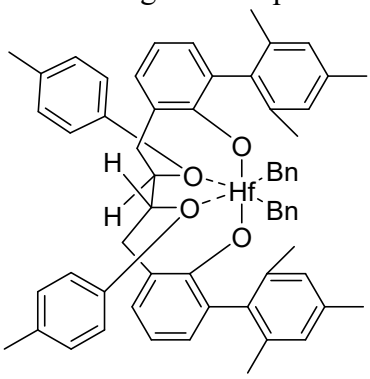
Metal−Ligand Complex 1



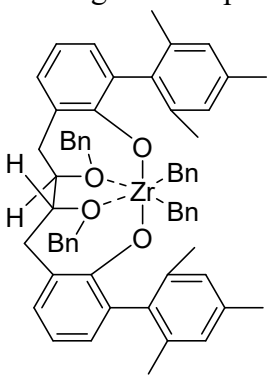
Metal−Ligand Complex 2



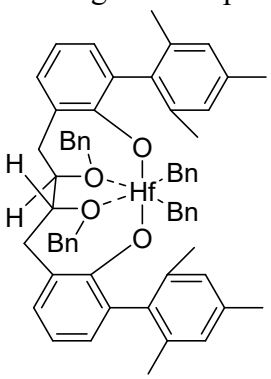
Metal−Ligand Complex 3



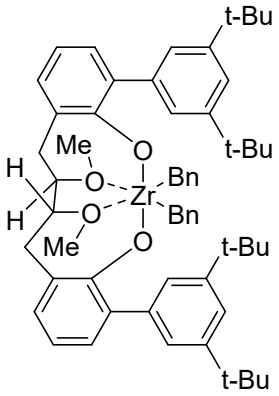
Metal−Ligand Complex 4



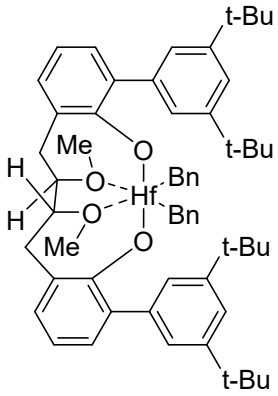
Metal−Ligand Complex 5



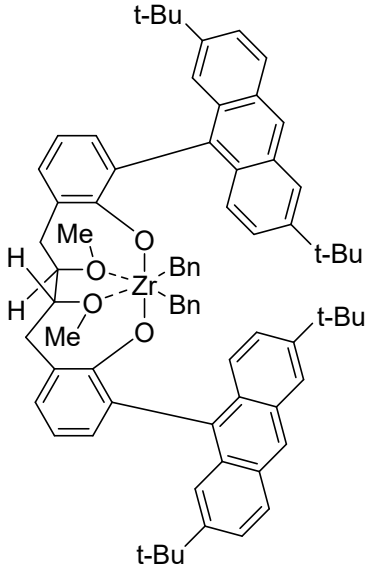
Metal−Ligand Complex 6



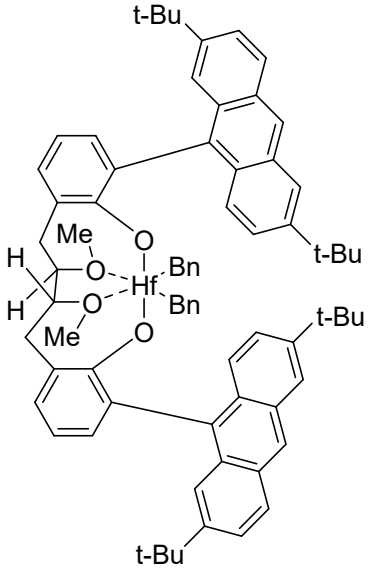
Metal−Ligand Complex 7



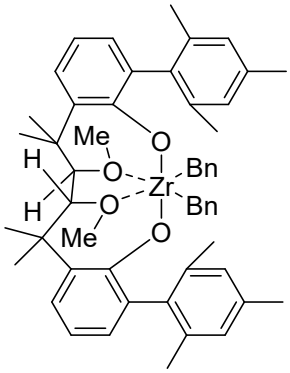
Metal−Ligand Complex 8



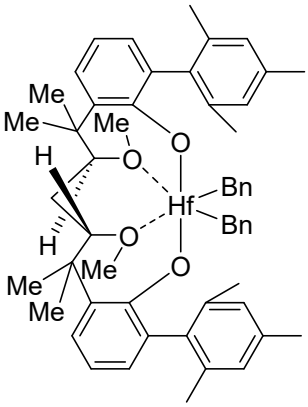
Metal−Ligand Complex 9



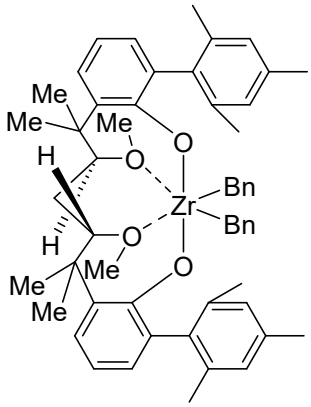
Metal−Ligand Complex 10



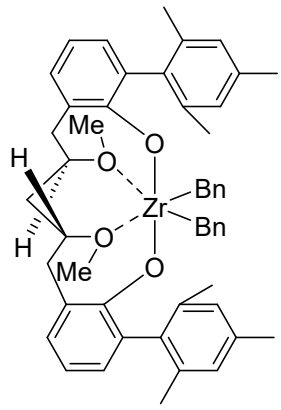
Metal−Ligand Complex 11



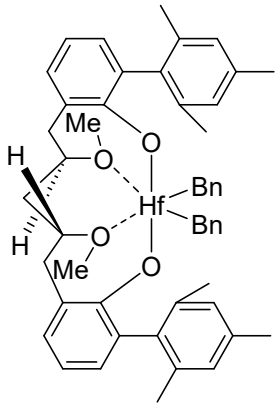
Metal−Ligand Complex 12



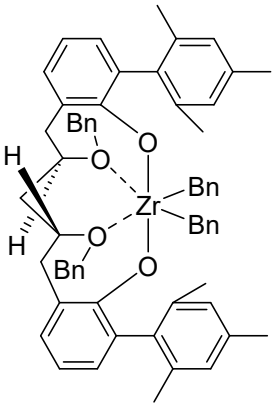
Metal−Ligand Complex 13



Metal−Ligand Complex 14



Metal−Ligand Complex 15



Metal−Ligand Complex 16