CATALYSTS AND METHODS FOR POLYMER SYNTHESIS

Priority Claim

This application claims priority to United States Provisional Patent Application Serial No. 61/091,013, filed August 22, 2008; United States Provisional Patent Application Serial No. 61/096,313, filed September 11, 2008 and United States Provisional Patent Application Serial No. 61/098,739, filed September 19, 2008. The entire contents of each of these priority applications are incorporated herein by reference.

Background

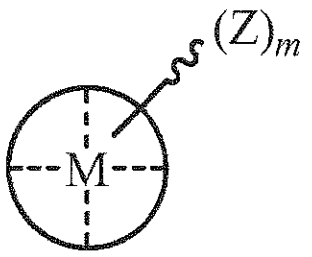
Catalysts capable of effecting the copolymerization of epoxides and carbon dioxide to form aliphatic polycarbonates (APCs) have been known in the art since the 1960s. The early catalysts were based on heterogeneous zinc compounds and suffered from low reactivity, a lack of selectivity for polymer formation vs. cyclic carbonate formation, and a tendency to produce polycarbonates contaminated with ether linkages.

Improved catalysts based on transition metals have been discovered over the past decade or so. These newer catalysts have increased reactivity and improved selectivity. Nevertheless, even using highly active catalysts such as those disclosed in US patent 7,304,172, the reaction times required to make high molecular weight polymer are typically quite long. In addition, the best-performing catalysts disclosed in the '172 patent require the addition of a separate co-catalyst to achieve optimum activity.

Attempts to address these shortcomings have been made. Catalysts described by Nozaki and co-workers (*Angew. Chem. Int. Ed.* **2006**, 45, 7274 -7277) tether an amine co-catalyst to a ligand of the catalyst. These next-generation catalytic systems suffer from lengthy and complicated syntheses and undesirable induction times prior to onset of polymerization. There remains a need for catalysts that have increased activity that will further reduce the polymerization time required to produce high molecular weight APCs.

Summary

In a first aspect of the present disclosure, there is provided a metal complex of the formula:

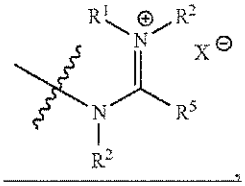


wherein:

M is cobalt;

 comprises a salen ligand; and

 represents one or more activating moieties tethered to the salen ligand, where  represents a linker moiety; *m* is an integer between 1 and 4 inclusive and represents the number of Z groups present on a linker moiety; and each (Z) represents an activating moiety comprising an amidine or amidinium group of the formula:



wherein

X^- is an anion;

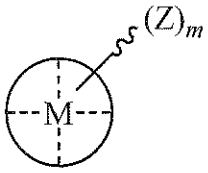
each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon

saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

In a second aspect of the present disclosure, there is provided a method for the synthesis of aliphatic polycarbonate polymers comprising the step of contacting one or more epoxides with carbon dioxide in the presence of a metal complex as described herein.

The present ~~invention~~disclosure provides, among other things, unimolecular catalyst systems having activity in the copolymerization of carbon dioxide and epoxides and methods of using the same. In some embodiments, the present ~~invention~~disclosure

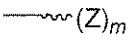
provides metal complexes having an activating species with co-catalytic activity tethered to a multidentate ligand that is coordinated to an active metal center of a metal complex. In certain embodiments, the present ~~invention~~disclosure provides unimolecular metal complexes and methods for using the same in the copolymerization of carbon dioxide and epoxides. In some embodiments, provided metal complexes have the structure:



wherein:

M is a metal atom;

 comprises a multidentate ligand;

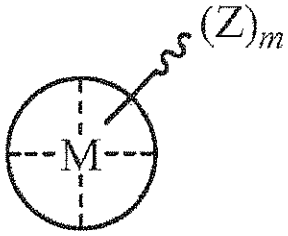
 represents one or more activating moieties attached to the multidentate ligand, where is a linker moiety covalently coupled to the ligand, each *Z* is an activating functional group; and m is an integer from 1 to 4 representing the number of *Z* groups present on an individual linker moiety.

In some embodiments, tethered activating functional groups (Z) are neutral nitrogen-containing moieties. In certain embodiments, neutral nitrogen-containing moieties are selected from the group consisting of:

CLAIMS

What is claimed is:

1. A metal complex of the formula:



wherein:

M is cobalt;

 comprises a salen ligand; and

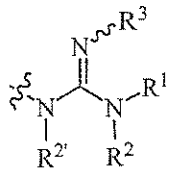
 represents one or more activating moieties tethered to the salen ligand, where represents a linker moiety; *m* represents the number of Z groups present on a linker moiety and is an integer between 1 and 4 inclusive; and

(i) each (Z) represents an activating moiety comprising a guanidine, guanidinium, amidine, or amidinium group; or

(ii) each (Z) represents an activating moiety comprising a neutral nitrogen-containing functional group or a cationic functional group, wherein the salen ligand has an activating moiety tethered to the position ortho to a metal-bound oxygen substituent of one or both of the salicylaldehyde-derived phenyl rings of the salen ligand.

2. The metal complex of claim 2, wherein Z comprises a guanidine group.

3. The metal complex of claim 2, where a guanidine group has a formula:



where each occurrence of R^1, R^2, $R^{2'}$, and R^3 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1, $R^{1'}$, R^2, $R^{2'}$, and R^3 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms.

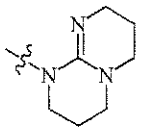
4. The metal complex of claim 2, wherein one or more of R^1, R^2, $R^{2'}$, and R^3, is H, or optionally substituted C_{1-6} aliphatic.

5. The metal complex of claim 3, wherein one or more of R^1, R^2, $R^{2'}$, and R^3, are methyl or ethyl.

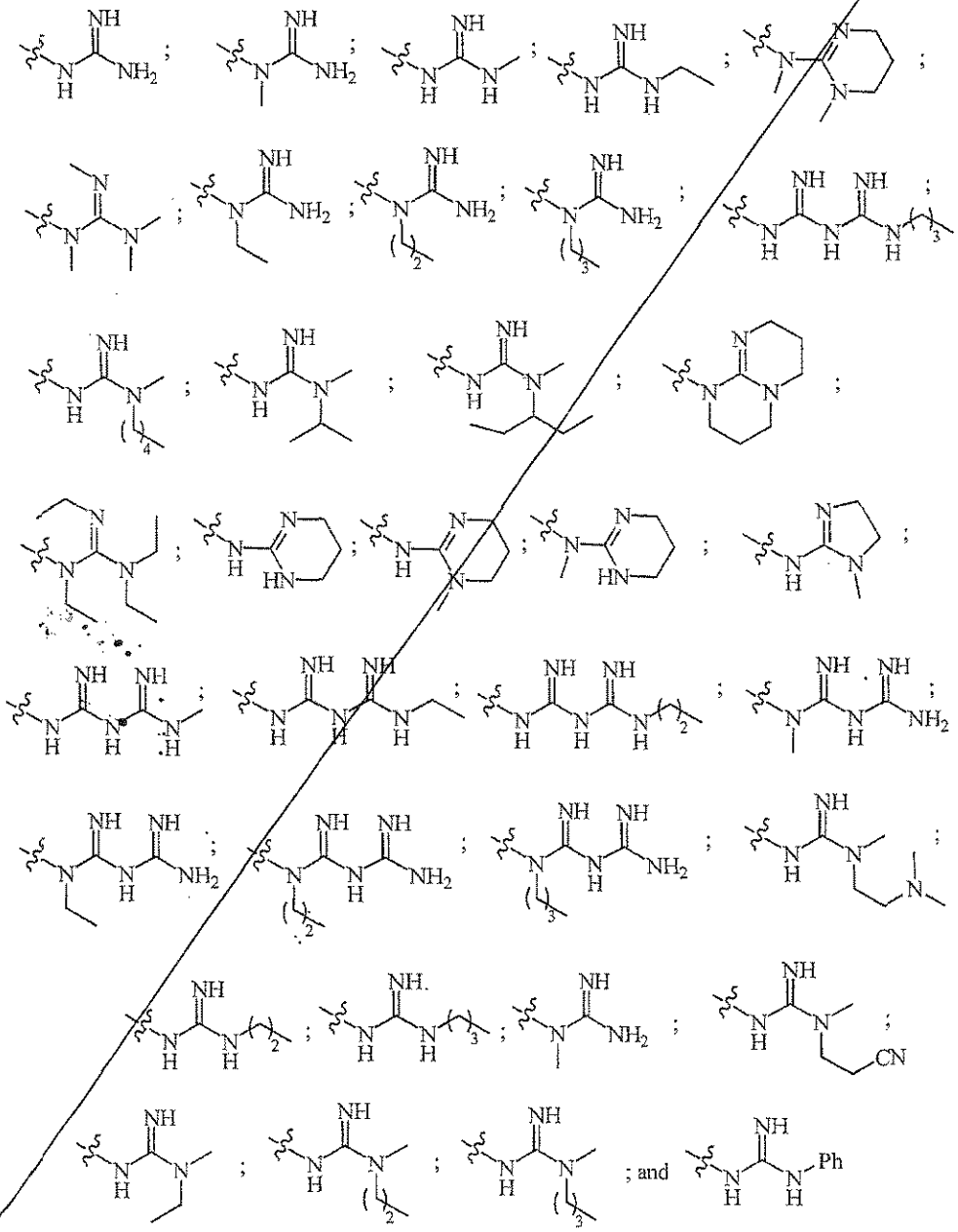
6. The metal complex of claim 2, wherein R^2 and $R^{2'}$ are taken together to form an optionally substituted ring.

7. The metal complex of claim 5, wherein R^1 and R^3 are taken together to form an optionally substituted ring.

8. The metal complex of claim 7, wherein the guanidine comprises:

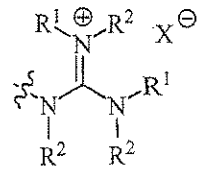


9. The metal complex of claim 1, wherein a guanidine is selected from the group consisting of:



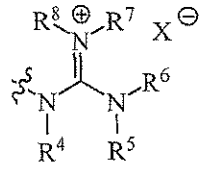
; and

10. The metal complex of claim 1, wherein the guanidinium group has a formula:



where each occurrence of R^1 and R^2 is independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic, C_{1-20} heteroaliphatic; phenyl, a 3- to 8-membered saturated or partially unsaturated monocylic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle, a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein two or more R^1 and R^2, groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms.

11. The metal complex of claim 10, wherein the guanidinium group has a formula:



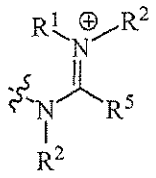
where each of R^4, R^5, R^6, R^7, and R^8 is independently hydrogen or C_{1-20} aliphatic, where any of (R^4 and R^5), (R^5 and R^6), (R^6 and R^7), (R^7 and R^8), and (R^4 and R^7) can be taken together with intervening atoms to form rings.

12. The metal complex of claim 11, wherein one or more of R^4, R^5, R^6, and R^7, is optionally substituted C_{1-12} aliphatic.

13. The metal complex of claim 11, wherein (R^4 and R^5) and (R^6 and R^7) are taken together to form rings.

14. The metal complex of claim 1, wherein the activating moiety comprises an amidinium group.

15. The metal complex of claim 14, wherein the amidinium group has a formula:



where each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially

unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

16. The metal complex of claim 15, wherein each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic group.

17. The metal complex of claim 15, wherein each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group.

18. The metal complex of claim 15, wherein R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings.

19. The metal complex of claim 18, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: –
$C(R^y)_2$-, $-C(R^y)_2C(R^y)_2$-, $-C(R^y)_2C(R^y)_2C(R^y)_2$-, $-C(R^y)_2OC(R^y)_2$-, and $-C(R^y)_2NR^yC(R^y)_2$-, wherein R^y is independently -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl, and where two or more adjacent R^{11} groups can be taken together to form an optionally substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms.

20. The metal complex of claim 19, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting
of: $-CH_2$-, $-CH_2CH_2$-, $-CH_2CH_2CH_2$-, $-CH_2OCH_2$-, and $-CH_2NR^yCH_2$-.

21. The metal complex of claim 19, wherein the resulting nitrogen-containing ring formed by the combination of R^1 and R^2 is partially unsaturated.

22. The metal complex of claim 19, wherein the resulting nitrogen-containing ring formed by the combination of R^1 and R^2 comprises a fused polycyclic heterocycle.

23. The metal complex of claim 15, wherein R^5 is H.

24. The metal complex of claim 15, wherein R^5 is optionally substituted C_{1-20} aliphatic.

25. The metal complex of claim 15, wherein R^5 is optionally substituted C_{1-6} aliphatic.

26. The metal complex of claim 15, wherein one or more R^1 or R^2 groups are taken together with R^5 and intervening atoms to form an optionally substituted ring.

27. The metal complex of claim 26, wherein R^1 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring.

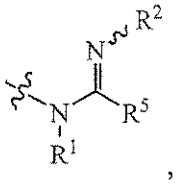
28. The metal complex of claim 26, wherein R^2 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring optionally containing one or more additional heteroatoms.

29. The metal complex of claim 15, wherein R^1, R^2 and R^5 are taken together to form an optionally substituted fused ring system.

30. The metal complex of claim 29, wherein a ring in the fused ring system formed by combinations of any of R^1, R^2 and R^5 is partially unsaturated or aromatic.

31. The metal complex of claim 1, wherein the activating moiety comprises an amidine.

32. The metal complex of claim 31, wherein the amidine has a formula:



,

where each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

33. The metal complex of claim 32, wherein each R^1 and R^2 is independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic.

34. The metal complex of claim 32, wherein R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic.

35. The metal complex of claim 32, wherein each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} aliphatic.

36. The metal complex of claim 32, wherein R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic.

37. The metal complex of claim 32, wherein R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl.

38. The metal complex of claim 32, wherein R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings.

39. The metal complex of claim 28, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: –
$C(R^y)_2$-, $-C(R^y)_2C(R^y)_2$-, $-C(R^y)_2C(R^y)_2C(R^y)_2$-, $-C(R^y)_2OC(R^y)_2$-, and $-C(R^y)_2NR^yC(R^y)_2$-.

40. The metal complex of claim 39, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2$-, $-CH_2CH_2$-, $-CH_2CH_2CH_2$-, $-CH_2OCH_2$-, and $-CH_2NR^yCH_2$-.

41. The metal complex of claim 32, wherein R^5 is H.

42. The metal complex of claim 32, wherein R^5 is optionally substituted C_{1-12} aliphatic.

43. The metal complex of claim 32, wherein R^5 is optionally substituted phenyl.

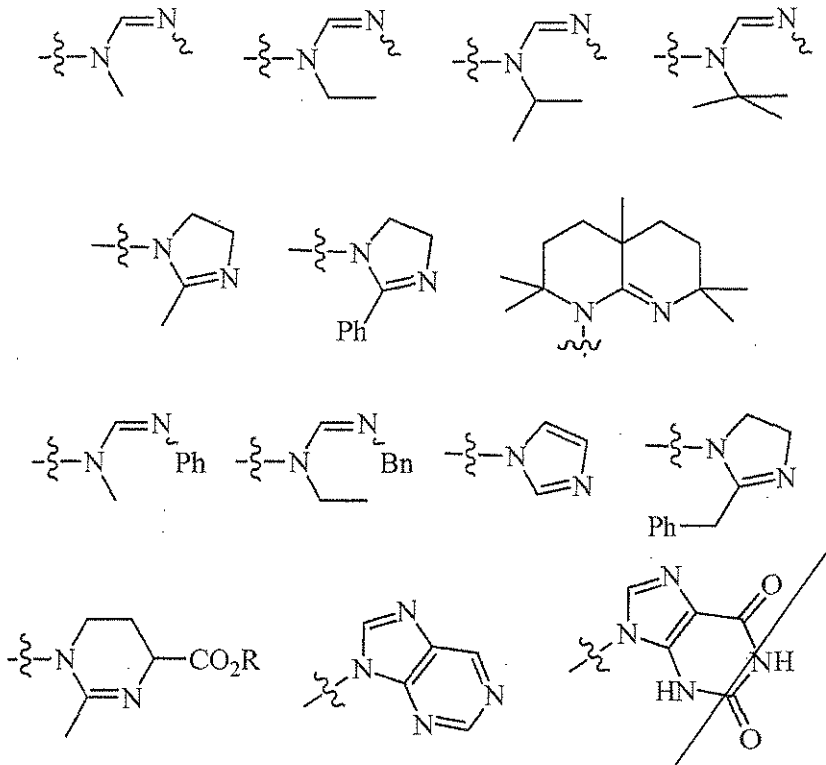
44. The metal complex of claim 32, wherein one or more R^1 or R^2 groups are taken together with R^5 and intervening atoms to form an optionally substituted ring.

45. The metal complex of claim 44, wherein R^1 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring.

46. The metal complex of claim 45, wherein R^1, R^2 and R^5 are taken together to form an optionally substituted fused ring system.

47. The metal complex of claim 46, wherein a ring formed by combinations of any of R^1, R^2 and R^5 is partially unsaturated or aromatic.

48. The metal complex of claim 32, wherein the amidine is selected from the group consisting of:

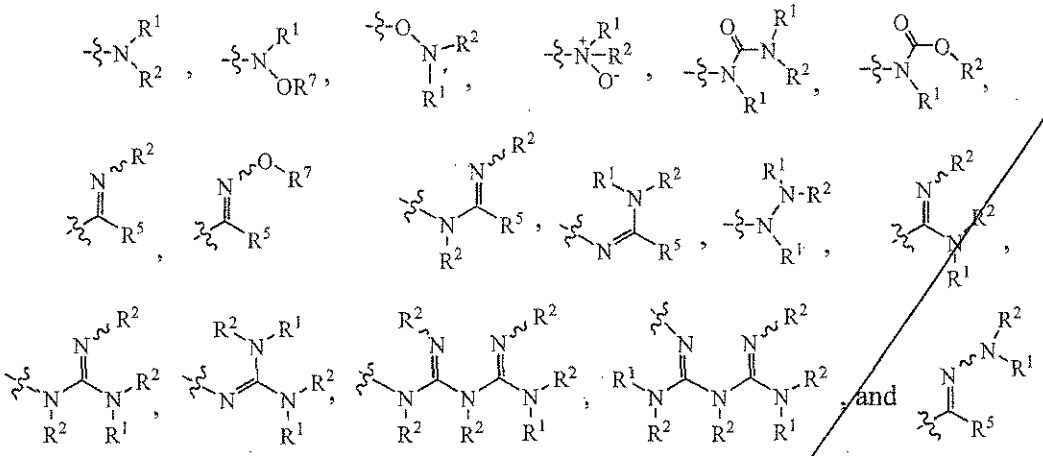


49. The metal complex of claim 1, wherein each (Z) represents an activating moiety comprising a neutral nitrogen-containing functional group, wherein the salen ligand has an activating moiety tethered to the position ortho to a metal-bound oxygen substituent of one or both of the salicylaldehyde-derived phenyl rings of the salen ligand.

50. The metal complex of claim 49, wherein the neutral nitrogen-containing functional group comprises an amidine.

51. The metal complex of claim 49, wherein the neutral nitrogen-containing functional group comprises a guanidine.

52. The metal complex of claim 49, wherein the neutral nitrogen-containing functional group is selected from the group consisting of:



or a combination of two or more of these,

wherein:

R^1 and R^2 is independently at each occurrence hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms;

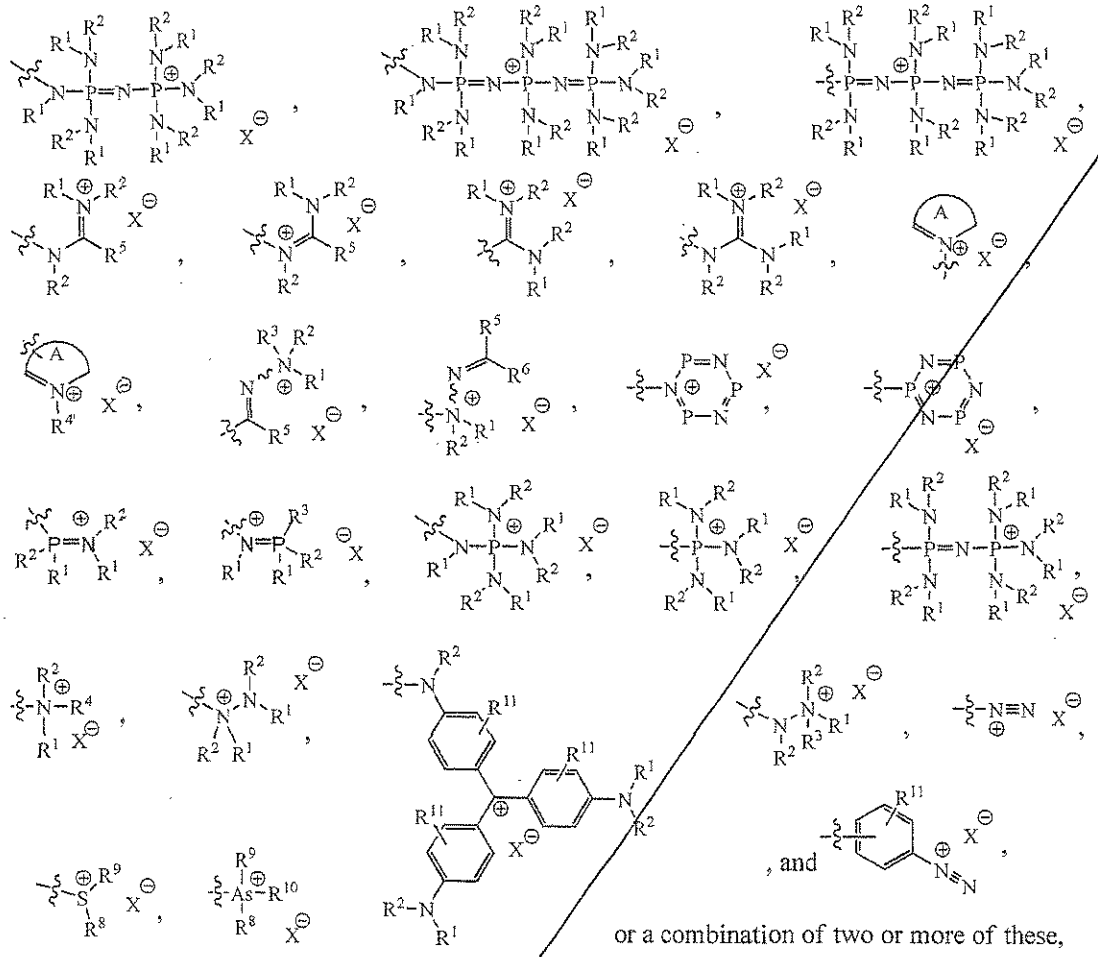
R^5 is independently at each occurrence hydrogen, or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen,

or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein an R^5 group can be taken with an R^1 or R^2 group to form one or more optionally substituted rings; and

R^7 is independently each occurrence, hydrogen, a hydroxyl protecting group, or an optionally substituted radical selected from the group consisting of C_{1-20} acyl; C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur.

53. The metal complex of claim 1, each (Z) represents an activating moiety comprising a cationic functional group, wherein the salen ligand has an activating moiety tethered to the position ortho to a metal-bound oxygen substituent of one or both of the salicylaldehyde-derived phenyl rings of the salen ligand.

54. The metal complex of claim 53, wherein Z is a cationic moiety selected from the group consisting of:



or a combination of two or more of these,

wherein:

R^1, R^2, and R^3 are independently at each occurrence hydrogen, or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1, R^2, and R^3 groups can

be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms;

R^4 is hydrogen or $-OR^7$;

$R^{4'}$ is hydrogen, hydroxyl, or optionally substituted C_{1-20} aliphatic;

R^5 and R^6 are independently at each occurrence, hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein R^5 and R^6 can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms, and an R^5 or R^6 group can be taken with an R^1 or R^2 group to form one or more optionally substituted rings;

R^7 is independently at each occurrence, hydrogen, a hydroxyl protecting group, or an optionally substituted radical selected from the group consisting of C_{1-20} acyl; C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur;

R^8, R^9, and R^{10} are independently at each occurrence, hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^8, R^9 and R^{10} groups can be taken together with intervening atoms to form one or more optionally substituted rings;

R^{11} is independently at each occurrence, selected from the group consisting of: halogen, $-NO_2$, -CN, $-SR^y$, $-S(O)R^y$, $-S(O)_2R^y$, $-NR^yC(O)R^y$, $-OC(O)R^y$, $-CO_2R^y$, -NCO, $-N_3$, $-OR^7$, $-OC(O)N(R^y)_2$, $-N(R^y)_2$, $-NR^yC(O)R^y$, $-NR^yC(O)OR^y$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where each occurrence of R^y is independently -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl, and where two or more adjacent R^{11} groups can be taken together to form an optionally

substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms;

X^- is any anion, and

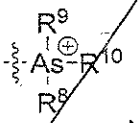
Ring A comprises an optionally substituted, 5- to 10-membered heteroaryl group.

55. The metal complex of claim 53, wherein the cationic moiety comprises a guanidinium group.

56. The metal complex of claim 53, wherein the cationic moiety comprises an amidinium group.

57. The metal complex of claim 53, wherein the cationic moiety comprises an arsonium group.

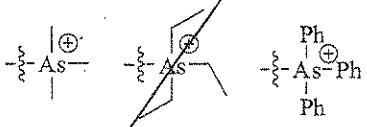
58. The metal complex of claim 57, wherein the arsonium group is:

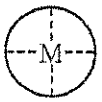


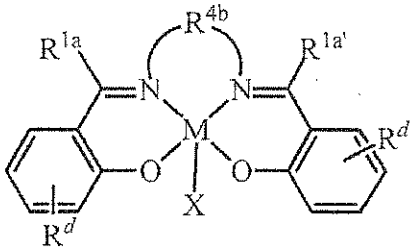
where R^8, R^9, and R^{10} are, independently at each occurrence, hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^8, R^9 and R^{10} groups can be taken together with intervening atoms to form one or more optionally substituted ringswhere each occurrence of R^8, R^9, and R^{10} is independently optionally substituted

C_{1-20} aliphatic. In some embodiments, each occurrence of R^8, R^9, and R^{10} is independently hydrogen or optionally substituted C_{1-20} heteroaliphatic. In some embodiments, each occurrence of R^9, R^{10}, and R^{11} is independently hydrogen or optionally substituted phenyl. In some embodiments, each occurrence of R^9, R^{10}, and R^{11} is independently hydrogen or optionally substituted 8- to 10-membered aryl. In some embodiments, each occurrence of R^8, R^9, and R^{10} is independently hydrogen or optionally substituted 5- to 10-membered heteroaryl. In some embodiments, each occurrence of R^9, R^{10}, and R^{11} is independently hydrogen or optionally substituted 3- to 7-membered heterocyclic. In some embodiments, R^8 and R^9 are taken together with intervening atoms to form one or more rings selected from the group consisting of: optionally substituted C_3-C_{14} carbocycle, optionally substituted 3- to 14-membered heterocycle, optionally substituted C_6-C_{10} aryl, and optionally substituted 5- to 10-membered heteroaryl.

59. The metal complex of claim 58, wherein the arsonium group is selected from the group consisting of:



60. The metal complex of any preceding claim, wherein  comprises:

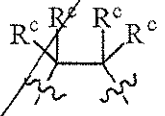


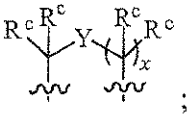
, where

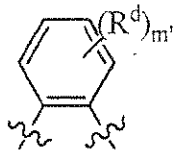
R^{1a} and $R^{1a'}$ are independently a $\sim\!\!\sim(Z)_m$ group, hydrogen, or an optionally substituted radical selected from the group consisting of: C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen and sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 atoms independently selected from nitrogen, oxygen and sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms selected from nitrogen, oxygen and sulfur;

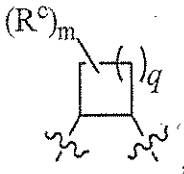
R^d at each occurrence is independently a $\sim\!\!\sim(Z)_m$ group, hydrogen, halogen, -OR, $-NR_2$, -SR, -CN, $-NO_2$, $-SO_2R$, -SOR, $-SO_2NR_2$; -CNO, $-NRSO_2R$, -NCO, $-N_3$, $-SiR_3$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^d groups may be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms,

R^{4b} is selected from the group consisting of:

a)  ;

b)  ;

c)  ; and

d)  , where

R^c at each occurrence is independently a $\sim\sim(Z)_m$ group, hydrogen, halogen, -OR, $-NR_2$, -SR, -CN, $-NO_2$, $-SO_2R$, -SOR, $-SO_2NR_2$; -CNO, $-NRSO_2R$, -NCO, $-N_3$, $-SiR_3$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^c groups may be taken together with the carbon atoms to which they are attached and any intervening atoms to form one or more optionally substituted rings; when two R^c groups are attached to the same carbon atom, they may optionally be taken together along with the carbon atom to which they are attached to form an optionally substituted moiety selected from the group consisting of: a 3- to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone, and an imine;

Y is a divalent linker selected from the group consisting of: -NR-, -N(R)C(O)-, -C(O)NR-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, $-SO_2-$, $-SiR_2-$, -C(=S)-, -C(=NR)-, or -N=N-; a polyether; a C_3 to C_8 substituted or unsubstituted carbocycle; and a C_1 to C_8 substituted or unsubstituted heterocycle;

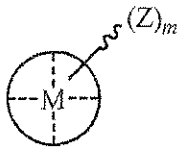
R at each occurrence is independently hydrogen, an optionally substituted radical selected the group consisting of acyl; C_{1-6} aliphatic; C_{1-6} heteroaliphatic;

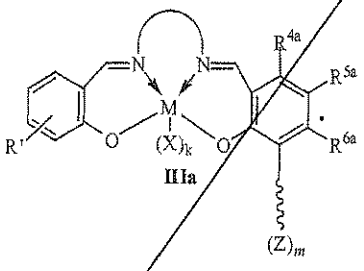
carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring,

m' is 0 or an integer from 1 to 4, inclusive;

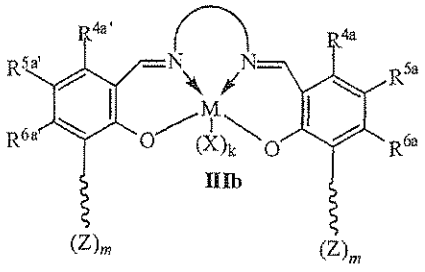
q is 0 or an integer from 1 to 4, inclusive; and

x is 0, 1, or 2.

61. The metal complex of any preceding claim, wherein , is selected from the group consisting of:



IIIa



IIIb

and

where  represents an optionally substituted moiety linking the two nitrogen atoms, and is selected from the group consisting of: phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently

selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an optionally substituted C_{2-20} aliphatic group, wherein one or more methylene units are optionally and independently replaced

by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, $-OC(O)N(R^y)-$, $-N(R^y)C(O)O-$, $-OC(O)O-$, $-O-$, $-C(O)-$, $-OC(O)-$, $-C(O)O-$, $-S-$, $-SO-$, $-SO_2-$, $-C(=S)-$, $-C(=NR^y)-$, $-C(=NOR^y)-$or $-N=N-$ where each occurrence of R^y is independently selected from the group consisting of hydrogen an optionally substituted C_{1-6} aliphatic group, and an optionally substituted aryl group;

R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, and $R^{6a'}$ are each independently a $\sim\!\!\sim(Z)_m$ group, hydrogen,

halogen, $-OR$, $-NR_2$, $-SR$, $-CN$, $-NO_2$, $-SO_2R$, $-SOR$, $-SO_2NR_2$; $-CNO$, $-NRSO_2R$, $-NCO$, $-N_3$, $-SiR_3$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two adjacent R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, and $R^{6a'}$ groups can be taken together with intervening atoms to form one or more optionally substituted rings,

R' represents one or more substituents optionally present on the phenyl ring and each R' is independently selected from the group consisting of:
halogen, $-NO_2$, -CN, $-SR^y$, $-S(O)R^y$, $-S(O)_2R^y$, $-NR^yC(O)R^y$, $-OC(O)R^y$, $-CO_2R^y$, -NCO, $-N_3$, $-OR^7$, $-OC(O)N(R^y)_2$, $-N(R^y)_2$, $-NR^yC(O)R^y$, $-NR^yC(O)OR^y$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur, where two or more adjacent R' groups can be taken together to form an optionally substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms;

R at each occurrence is independently hydrogen, an optionally substituted radical selected the group consisting of acyl; C_{1-6} aliphatic; C_{1-6} heteroaliphatic; carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen

atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring,

R^y is -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl;

R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, $R^{6a'}$, R^{7a}, and $R^{7a'}$ are each independently a $\sim\!\!\sim$ Z group, hydrogen,

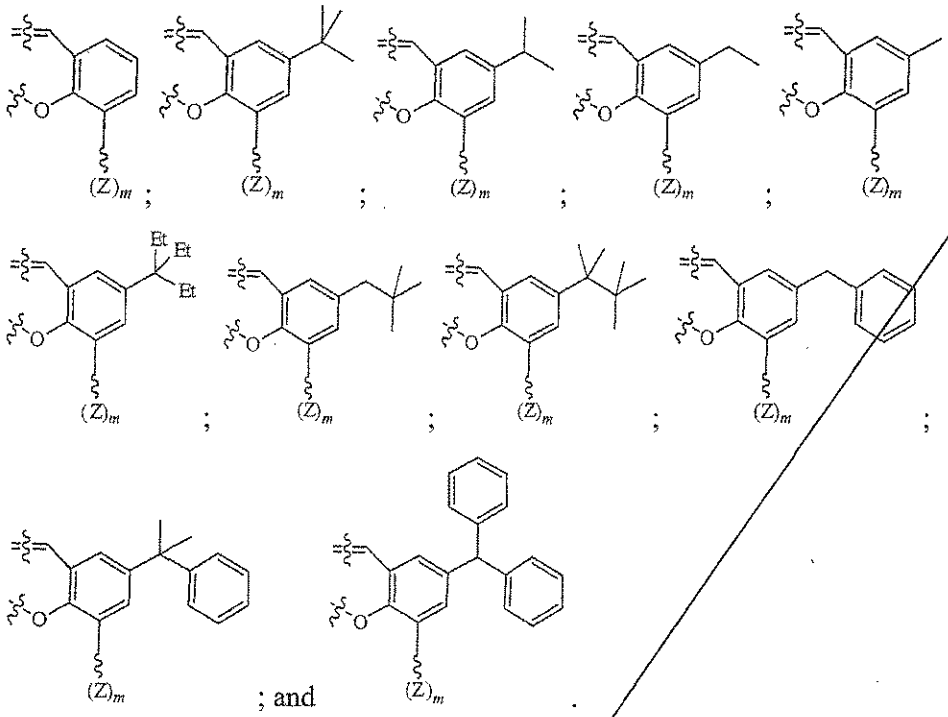
halogen, -OR, $-NR_2$, -SR, -CN, $-NO_2$, $-SO_2R$, -SOR, $-SO_2NR_2$; -CNO, $-NRSO_2R$, -NCO, $-N_3$, $-SiR_3$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where any two adjacent R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, and $R^{6a'}$ groups can be taken together with intervening atoms to form one or more optionally substituted rings;

n is 0 or an integer from 1 to 8, inclusive;

p is 0 or an integer from 1 to 4, inclusive; and

k is 1.

62. The metal complex of any preceding claim, wherein the metal complex comprises a substructure conforming to a formula selected from the group consisting of:



; and

63. The metal complex of any preceding claim, wherein ——〰 comprises an optionally substituted C_{2-30} aliphatic group wherein one or more methylene units are optionally and independently replaced by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, $-O-$, $-C(O)-$, $-OC(O)-$, $-C(O)O-$, $-S-$, $-SO-$, $-SO_2-$, $-C(=S)-$, $-C(=NR^y)-$, or $-N=N-$, where each occurrence of R^y is independently -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl.

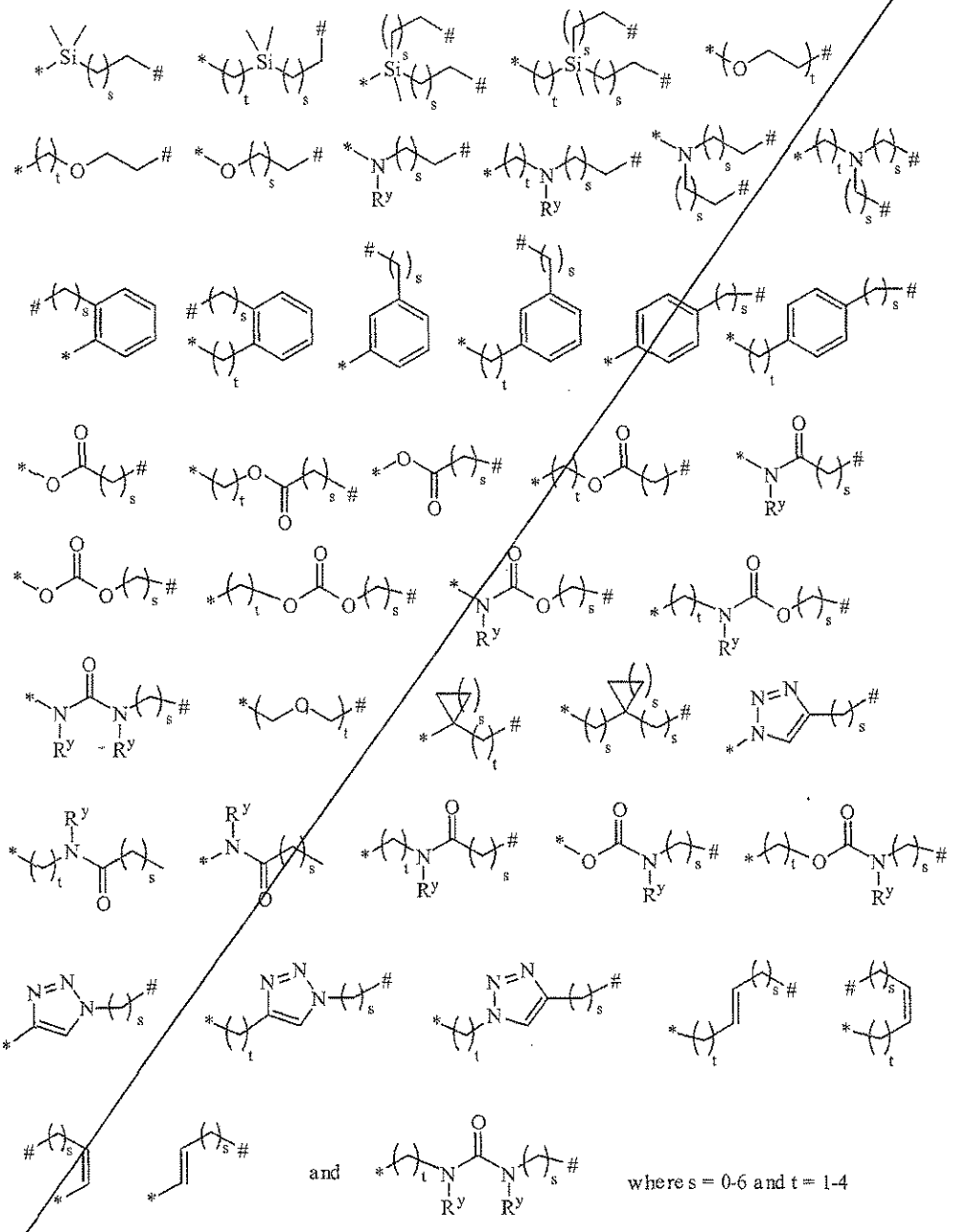
64. The metal complex of claim 63, wherein ——〰 comprises an optionally substituted C_{3-30} aliphatic group.

65. The metal complex of claim 63, wherein ——〰 comprises an optionally substituted C_{4-8} aliphatic group.

66. The metal complex of claim 63, wherein ——〰 comprises an optionally substituted C_3 aliphatic group.

67. The metal complex of claim 63, wherein the linker "——〰" comprises an optionally substituted straight alkyl chain.

68. The metal complex of claim 63, wherein ——∿∿ is selected from the group consisting of:



where * represents the site of attachment to the ligand, and each # represents a site of attachment the activating group, and

R^y is independently at each occurrence, -H or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl, where two or more adjacent R^{11} groups can be taken together to form an optionally substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms..

69. The metal complex of claim 60, wherein X is selected from the group consisting of: chlorine, bromine, an optionally substituted C_{1-12} carboxylate, azide, an optionally substituted phenoxide, and sulfonate.

70. The metal complex of claim 60, wherein X is selected from the group consisting of: chloride, acetate, trifluoroacetate, azide, pentafluorobenzoate, and a nitrophenolate.

71. The metal complex of any preceding claim, wherein the cobalt has an oxidation state of 3+.

72. The metal complex of any preceding claim, wherein there are activating moieties tethered to the positions ortho and para to the phenolic oxygen of one or both of the salicylaldehyde-derived phenyl rings of a salen ligand.

73. The metal complex of any preceding claim, wherein *m* is 1.

74. The metal complex of any preceding claim, wherein *m* is greater than 1.

75. A polymerization method comprising the step of contacting one or more epoxides with carbon dioxide in the presence of an effective amount of a metal complex of any preceding claim to form a polycarbonate.

76. The polymerization method of claim 75, wherein the epoxide is selected from the group consisting of: ethylene oxide, propylene oxide, butylene oxide, cyclohexene oxide, 1,2 octene oxide, 3-vinyl cyclohexene oxide, epichlorohydrin and mixtures of any two or more of these.

77. The polymerization method of claim 75, wherein the epoxide is ethylene oxide, propylene oxide, or cyclohexene oxide.

78. The polymerization method of claim 75, wherein the epoxide is ethylene oxide.

79. The polymerization method of claim 75, wherein the epoxide is propylene oxide.

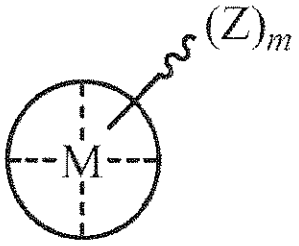
80. The polymerization method of claim 75, wherein a pressure of carbon dioxide is between about 50 and 800 psi.

81. The polymerization method of claim 75, wherein a molar ratio of metal complex to epoxide is between about 1:1000 and about 1:100,000.

CLAIMS

What is claimed is:

1. A metal complex of the formula:



,

wherein:

M is cobalt;

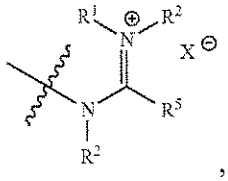
 comprises a salen ligand; and

 represents one or more activating moieties tethered to the salen ligand, where  represents a linker moiety;

m is an integer between 1 and 4 inclusive and represents the number of Z groups present on a linker moiety;

and

each (Z) represents an activating moiety comprising an amidine or amidinium group of the formula:



,

wherein

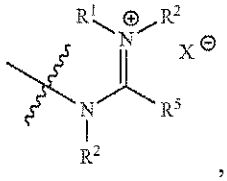
X^- is an anion;

each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form

one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

2. The metal complex of claim 1, wherein the activating moiety comprises an amidinium group of the formula:



wherein X^-, R^1, R^2, and R^5 are as defined in claim 1.

3. The metal complex of claim 1, wherein each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-20} aliphatic group.

4. The metal complex of claim 1, wherein each occurrence of R^1 and R^2 is independently an optionally substituted phenyl group.

5. The metal complex of claim 1, wherein R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings.

6. The metal complex of claim 5, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$, wherein each occurrence of R^y is independently -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl.

7. The metal complex of claim 6, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2OCH_2-$, and $-CH_2NR^yCH_2-$.

8. The metal complex of claim 7, wherein the resulting nitrogen-containing ring formed by the combination of R^1 and R^2 is partially unsaturated.

9. The metal complex of claim 7, wherein the resulting nitrogen-containing ring formed by the combination of R^1 and R^2 comprises a fused polycyclic heterocycle.

10. The metal complex of claim 1, wherein R^5 is H.

11. The metal complex of claim 1, wherein R^5 is optionally substituted C_{1-20} aliphatic.

12. The metal complex of claim 1, wherein R^5 is optionally substituted C_{1-6} aliphatic.

13. The metal complex of claim 1, wherein one or more R^1 or R^2 groups are taken together with R^5 and intervening atoms to form an optionally substituted ring.

14. The metal complex of claim 13, wherein R^1 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring.

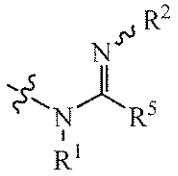
15. The metal complex of claim 13, wherein R^2 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring optionally containing one or more additional heteroatoms.

16. The metal complex of claim 1, wherein R^1, R^2 and R^5 are taken together to form an optionally substituted fused ring system.

17. The metal complex of claim 16, wherein a ring in the fused ring system formed by combinations of any of R^1, R^2 and R^5 is partially unsaturated or aromatic.

18. The metal complex of claim 1, wherein the activating moiety comprises an amidine.

19. The metal complex of claim 18, wherein the amidine has a formula:



where each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

20. The metal complex of claim 19, wherein each R^1 and R^2 is independently an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic, 5- to 14-membered heteroaryl, phenyl, 8- to 10-membered aryl and 3- to 7-membered heterocyclic.

21. The metal complex of claim 19, wherein R^1 and R^2 are each independently an optionally substituted radical selected from the group consisting of C_{1-12} aliphatic and C_{1-12} heteroaliphatic.

22. The metal complex of claim 19, wherein each occurrence of R^1 and R^2 is independently an optionally substituted C_{1-12} aliphatic.

23. The metal complex of claim 19, wherein R^1 and R^2 are each independently optionally substituted C_{1-6} aliphatic.

24. The metal complex of claim 19, wherein R^1 and R^2 are both methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, phenyl or benzyl.

25. The metal complex of claim 19, wherein R^1 and R^2 are taken together with intervening atoms to form one or more optionally substituted rings.

26. The metal complex of claim 25, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-C(R^y)_2-$, $-C(R^y)_2C(R^y)_2-$, $-C(R^y)_2C(R^y)_2C(R^y)_2-$, $-C(R^y)_2OC(R^y)_2-$, and $-C(R^y)_2NR^yC(R^y)_2-$, wherein each occurrence of R^y is independently -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl.

27. The metal complex of claim 26, wherein R^1 and R^2 are taken together to form a ring fragment selected from the group consisting of: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2OCH_2-$, and $-CH_2NR^yCH_2-$.

28. The metal complex of claim 19, wherein R^5 is H.

29. The metal complex of claim 19, wherein R^5 is optionally substituted C_{1-12} aliphatic.

30. The metal complex of claim 19, wherein R^5 is optionally substituted phenyl.

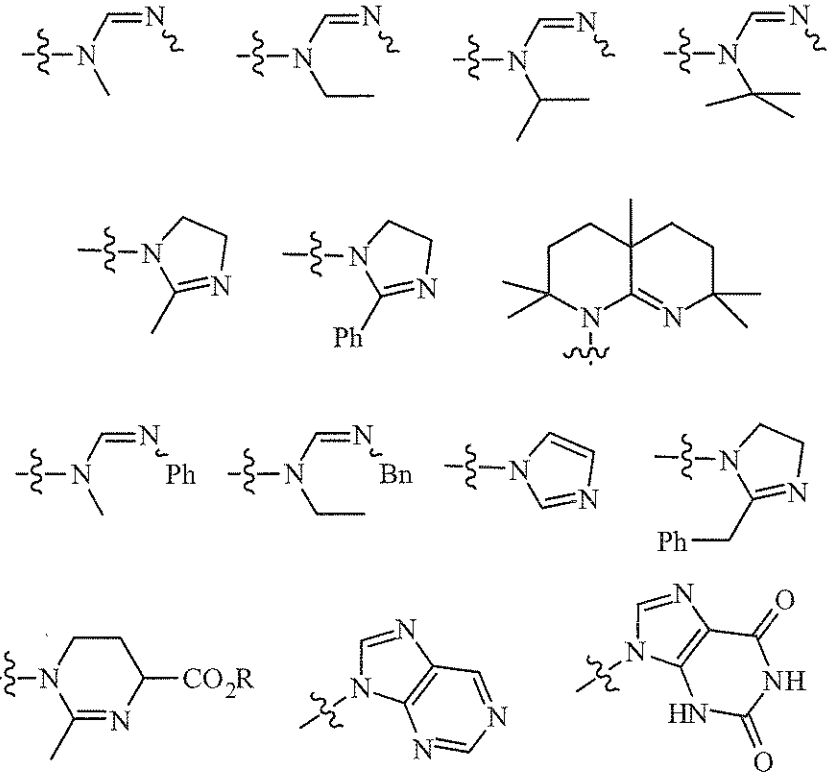
31. The metal complex of claim 19, wherein one or more R^1 or R^2 groups are taken together with R^5 and intervening atoms to form an optionally substituted ring.

32. The metal complex of claim 31, wherein R^1 and R^5 are taken together to form an optionally substituted 5- or 6-membered ring.

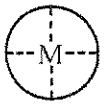
33. The metal complex of claim 32, wherein R^1, R^2 and R^5 are taken together to form an optionally substituted fused ring system.

34. The metal complex of claim 33, wherein a ring formed by combinations of any of R^1, R^2 and R^5 is partially unsaturated or aromatic.

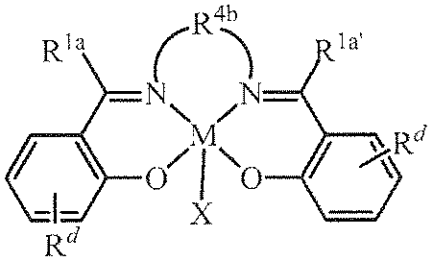
35. The metal complex of claim 19, wherein the amidine is selected from the group consisting of:



36. The metal complex of claim 1, wherein



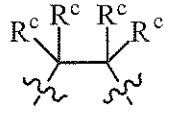
comprises:

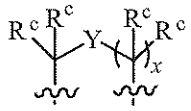


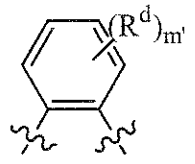
R^{1a} and $R^{1a'}$ are independently a $\sim\!\!\sim(Z)_m$ group, hydrogen, or an optionally substituted radical selected from the group consisting of: C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen and sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 atoms independently selected from nitrogen, oxygen and sulfur; and a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms selected from nitrogen, oxygen and sulfur;

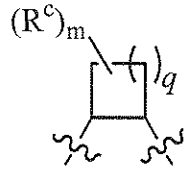
R^d at each occurrence is independently a $\sim\!\!\sim(Z)_m$ group, hydrogen, halogen, -OR, $-NR_2$, -SR, -CN, $-NO_2$, $-SO_2R$, -SOR, $-SO_2NR_2$; -CNO, $-NRSO_2R$, -NCO, $-N_3$, $-SiR_3$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle; a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^d groups may be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more heteroatoms,

R^{4b} is selected from the group consisting of:

a)  ;

b)  ;

c)  ; and

d)  ,

where

R^c at each occurrence is independently a $\sim\!\!\sim(Z)_m$ group, hydrogen, halogen, -OR, -NR_2, -SR, -CN, -NO_2, -SO_2R, -SOR, -SO_2NR_2; -CNO, -$NRSO_2R$, -NCO, -N_3, -SiR_3; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; where two or more R^c groups may be taken together with the carbon atoms to which they are attached and any intervening atoms to form one or more optionally substituted rings; when two R^c groups are attached to the same carbon atom, they may optionally be taken together along with the carbon atom to which they are attached to form an optionally substituted moiety selected from the group consisting of: a 3- to 8-membered spirocyclic ring, a carbonyl, an oxime, a hydrazone, and an imine;

Y is a divalent linker selected from the group consisting of: -NR-, -N(R)C(O)-, -C(O)NR-, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, -SO_2-, -SiR_2-, -C(=S)-, -C(=NR)-, or -N=N-; a polyether; a C_3 to C_8 substituted or unsubstituted carbocycle; and a C_1 to C_8 substituted or unsubstituted heterocycle;

R at each occurrence is independently hydrogen, an optionally substituted radical selected the group consisting of acyl; C_{1-6} aliphatic; C_{1-6} heteroaliphatic; carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring,

X' is a nucleophile capable of ring opening an epoxide;

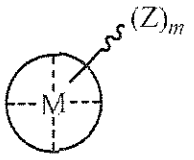
m' is 0 or an integer from 1 to 4, inclusive;

m'' is 0 or an integer from 1 to 6, inclusive;

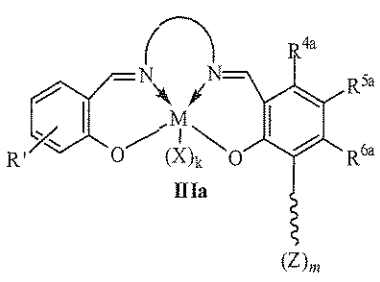
q is 0 or an integer from 1 to 4, inclusive; and

x is 0, 1, or 2.

37. The metal complex of claim 1, wherein

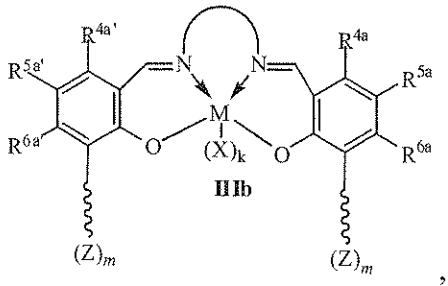


, is selected from the group consisting of:



IIIa

and



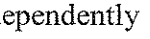
IIIb

,

where



represents an optionally substituted moiety linking the two nitrogen atoms, and is selected from the group consisting of: phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; or an optionally substituted C_{2-20} aliphatic group, wherein one or more methylene units are optionally and independently replaced by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, $-OC(O)N(R^y)-$, $-N(R^y)C(O)O-$, $-OC(O)O-$, $-O-$, $-C(O)-$, $-OC(O)-$, $-C(O)O-$, $-S-$, $-SO-$, $-SO_2-$, $-C(=S)-$, $-C(=NR^y)-$, $-C(=NOR^y)-$ or $-N=N-$;

R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, and $R^{6a'}$ are each independently a  group, hydrogen,
halogen, $-OR$, $-NR_2$, $-SR$, $-CN$, $-NO_2$, $-SO_2R$, $-SOR$, $-SO_2NR_2$; $-CNO$, $-NRSO_2R$, $-NCO$, $-N_3$, $-SiR_3$; or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon

saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two adjacent R^{4a}, $R^{4a'}$, R^{5a}, $R^{5a'}$, R^{6a}, and $R^{6a'}$ groups can be taken together with intervening atoms to form one or more optionally substituted rings,

R' represents one or more substituents optionally present on the phenyl ring and each R' is independently selected from the group consisting of: halogen, $-NO_2$, -CN, $-SR^y$, $-S(O)R^y$, $-S(O)_2R^y$, $-NR^yC(O)R^y$, $-OC(O)R^y$, $-CO_2R^y$, -NCO, $-N_3$, $-OR^7$, $-OC(O)N(R^y)_2$, $-N(R^y)_2$, $-NR^yC(O)R^3$, $-NR^yC(O)OR^y$; and an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur, where two or more adjacent R' groups can be taken together to form an optionally substituted saturated, partially unsaturated, or aromatic 5- to 12-membered ring containing 0 to 4 heteroatoms;

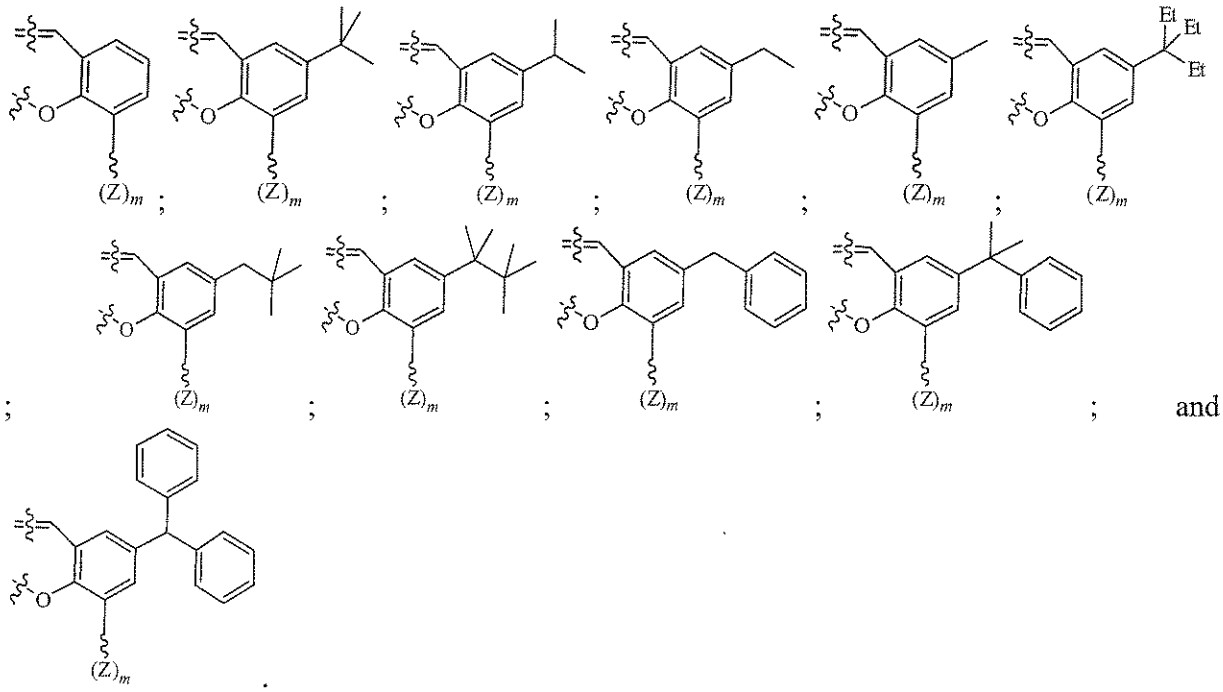
R at each occurrence is independently hydrogen, an optionally substituted radical selected the group consisting of acyl; C_{1-6} aliphatic; C_{1-6} heteroaliphatic; carbamoyl; arylalkyl; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; an oxygen protecting group; and a nitrogen protecting group, where two R groups on the same nitrogen atom can optionally be taken together to form an optionally substituted 3- to 7-membered ring;

R^y is -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic, 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl;

X' is a nucleophile capable of ring opening an epoxide; and

k is 1.

38. The metal complex of claim 37, wherein the metal complex comprises a substructure conforming to a formula selected from the group consisting of:



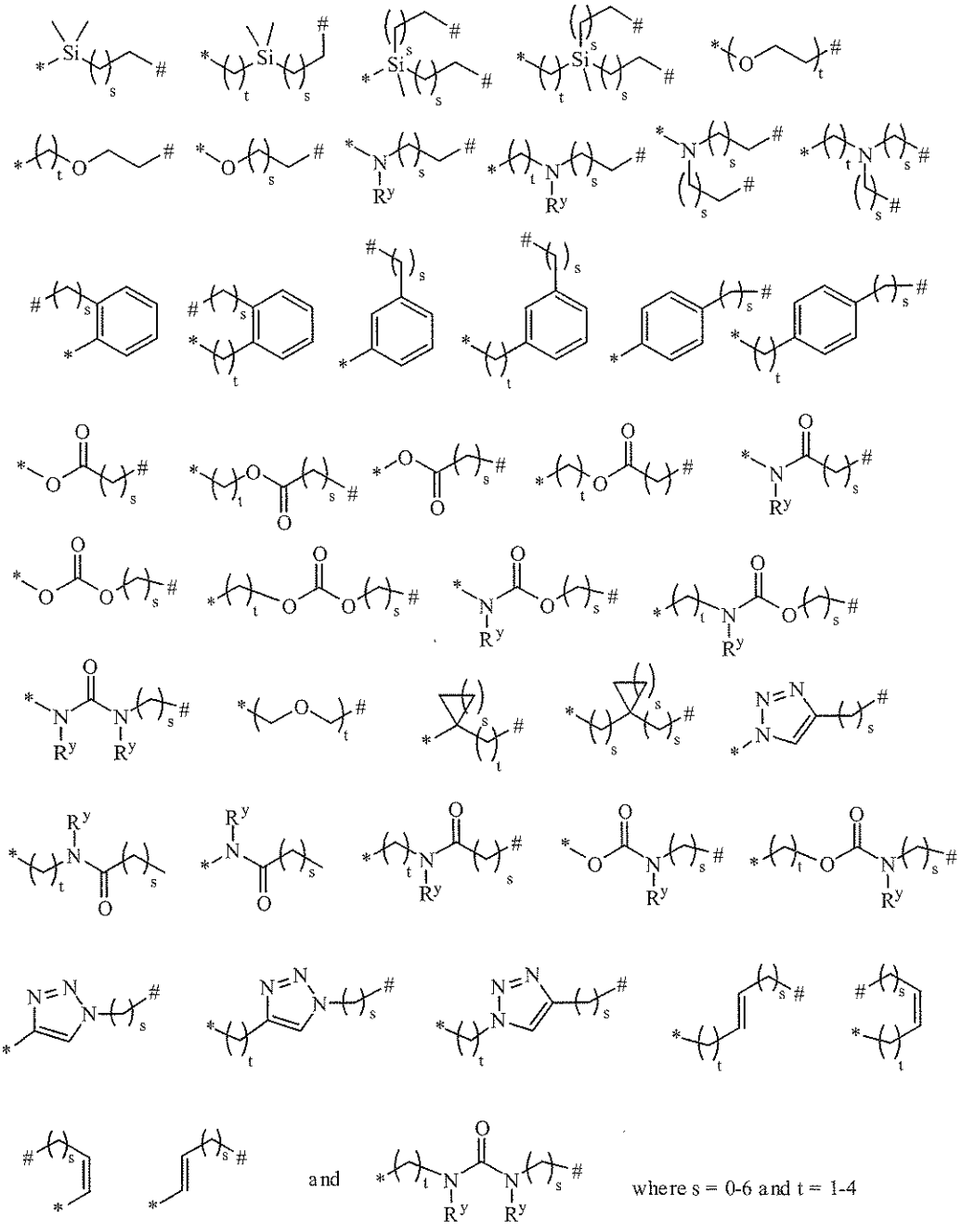
39. The metal complex of claim 38, wherein ——〰 comprises an optionally substituted C_{2-30} aliphatic group wherein one or more methylene units are optionally and independently replaced
by $-NR^y-$, $-N(R^y)C(O)-$, $-C(O)N(R^y)-$, -O-, -C(O)-, -OC(O)-, -C(O)O-, -S-, -SO-, $-SO_2-$, $-C(=S)-$, $-C(=NR^y)-$, or -N=N-, where each occurrence of R^y is independently -H, or an optionally substituted radical selected from the group consisting of C_{1-6} aliphatic 3- to 7-membered heterocyclic, phenyl, and 8- to 10- membered aryl.

40. The metal complex of claim 38, wherein ——〰 comprises a C_{3-30} aliphatic group.

41. The metal complex of claim 38, wherein ——〰 comprises a C_{4-8} aliphatic group.

42. The metal complex of claim 38, wherein ——〰 comprises a C_3 aliphatic group.

43. The metal complex of claim 38, wherein —〰— is selected from the group consisting of:



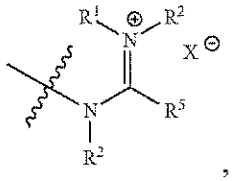
where * represents the site of attachment to the ligand, and each # represents a site of attachment to the amidine or amidinium activating moiety.

44. The metal complex of claim 36, wherein X' is selected from the group consisting of: chlorine, bromine, an optionally substituted C_{1-12} carboxylate, azide, an optionally substituted phenoxide, and sulfonate.

45. The metal complex of claim 36, wherein X' is selected from the group consisting of: chloride, acetate, trifluoroacetate, azide, pentafluorobenzoate, and a nitrophenolate.

46. A method for the synthesis of aliphatic polycarbonate polymers comprising the step of contacting one or more epoxides with carbon dioxide in the presence of a metal complex of claim 1.

47. The method of claim 46, wherein the activating moiety comprises an amidinium group of the formula:



,

wherein

X^- is an anion;

each of R^1 and R^2 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; wherein any two or more R^1 and R^2 groups can be taken together with intervening atoms to form one or more optionally substituted rings optionally containing one or more additional heteroatoms; and

each occurrence of R^5 is independently hydrogen or an optionally substituted radical selected from the group consisting of C_{1-20} aliphatic; C_{1-20} heteroaliphatic; phenyl; a 3- to 8-membered saturated or partially unsaturated monocyclic carbocycle, a 7-14 carbon saturated, partially unsaturated or aromatic polycyclic carbocycle; a 5- to 6-membered monocyclic heteroaryl ring having 1-4 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 3- to 8-membered saturated or partially unsaturated heterocyclic ring having 1-3 heteroatoms independently selected from nitrogen, oxygen, or sulfur; a 6- to 12-membered polycyclic saturated or partially unsaturated heterocycle having 1-5 heteroatoms independently selected from nitrogen, oxygen, or sulfur; and an 8- to 10-membered bicyclic heteroaryl ring having

1-5 R^5 can be taken with an R^1 or R^2 group to form one or more optionally substituted rings.

48. The method of claim 46, wherein the activating moiety comprises an amidine group.

49. The method of claim 46, wherein the epoxide is ethylene oxide, propylene oxide, or cyclohexene oxide.

50. The method of claim 46, wherein the epoxide is ethylene oxide.

51. The method of claim 46, wherein the epoxide is propylene oxide.

52. The method of claim 46, wherein a pressure of carbon dioxide is between about 50 and 800 psi.

53. The method of claim 46, wherein a molar ratio of complex to epoxide is between about 1:1000 and about 1:100,000.