CLAIMS

We claim:

1. A method of preparing a poly-unsaturated cyclic polymer, comprising:

providing catalyst consisting of a trianionic pincer ligand supported metal-alkylidyne complex or a tetra-anionic pincer-ligand supported metal-alkyne or a tetra-anionic pincer-ligand supported metallacycloalkylene complex;

providing a multiplicity of an alkyne monomers; and

mixing the alkyne monomers with the catalyst wherein the alkyne monomers polymerizes to a poly-unsaturated cyclic polymer.

2. The method of claim 1, wherein the catalyst is [^{t}BuOCO]W≡CC(CH$_3$)$_3$(THF)$_2$ (**1**), [O$_2$C(^{t}BuC=)W(η^2-HC≡CPh)] (**2**), [O$_2$C(PhC=)W(η^2-HC≡C^{t}Bu)] (**3**), or [O$_2$C(^{t}BuC=)W(η^2-HC≡ C^{t}Bu)] (**4**).

3. The method of claim 1, wherein the catalyst is [O$_2$C(^{t}BuC=)W(η^2-HC≡ C^{t}Bu)] (**4**).

4. The method of claim 1, further comprising an aprotic solvent.

5. The method of claim 1, wherein the alkyne monomer is phenylacetylene.

6. The method of claim 1, wherein the poly-unsaturated cyclic polymer is free of linear impuries.

7. A method of preparing a saturated cyclic polymer, comprising:

preparing a poly-unsaturated cyclic polymer by the method of claim 1; and

hydrogenating the poly-unsaturated cyclic polymer to form a saturated cyclic polymer.

8. The method of claim 7, wherein the poly-unsaturated cyclic polymer is cyclic polyphenylacetylene and the saturated cyclic polymer is poly(styrene).

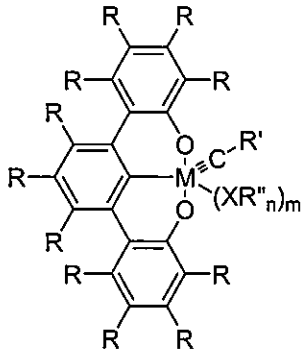
9. A method of preparing $[O_2C(^tBuC=)W(\eta^2\text{-}HC\equiv C^tBu)]$ (**4**); comprising:

providing $[^tBuOCO]W\equiv CC(CH_3)_3(THF)_2$ (**1**); and

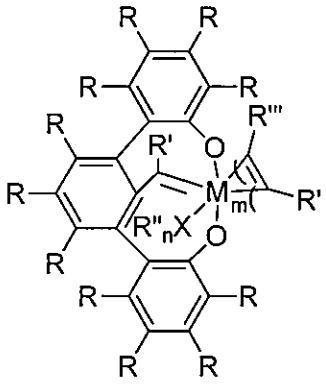
mixing the $[^tBuOCO]W\equiv CC(CH_3)_3(THF)_2$ (**1**) with about five equivalents of 3,3-dimethyl-1-butyne (HCC^tBu), wherein $[O_2C(^tBuC=)W(\eta^2\text{-}HC\equiv C^tBu)]$ (**4**) is formed.

CLAIMS

1. A tridentate pincer ligand supported metal complex, comprising the structure:



where: M is a group 5-7 transition metal; R is independently, H, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, or C_5 to C_{20} alkyl: R' is methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl *t*-butyl, C_5 to C_{20} alkyl, phenyl, naphthyl, or C_{13} to C_{22} aryl; X is independently O, N, S, P, or Se; n is independently 1 to 2, m is 1 to 2, and R" is independently methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, C_5 to C_{20} alkyl, phenyl, naphthyl, C_{13} to C_{18} aryl or two R" are combined as a C_4 to C_6 alkylene, wherein $XR"_2$ is a 5 to 7-membered ring; or



where: R is, independently, H, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl *t*-butyl, or larger alkyl; R' is, independently, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, C_5-C_{22} alkyl, phenyl, naphthyl, C_{13}-C_{22} aryl, aryl substituted with one or more fluoro, C_1-C_3 alkoxy, or trifluoromethyl, or trimethylsilyl; R"' is H or methyl; X, independently, is O, N, S, P, or Se; R", independently, is methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, C_5-C_{22}, phenyl, naphthyl, C_{13}-C_{22} aryl, or two R" are combined as a C_4 to C_6 alkylene; n is 1 to 3 depending on X; m is 1 to 2; and M is a group 5-7 transition metal.

2. The tridentate pincer ligand supported metal complex of claim 1, wherein M is W.

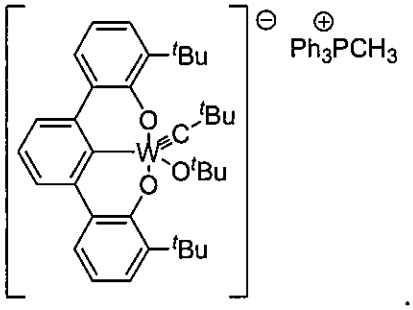
3. The tridentate pincer ligand supported metal complex of claim 1, wherein R is alkyl in the 3 and 3" positions and H in all other positions.

4. The tridentate pincer ligand supported metal complex of claim 1, wherein X is O.

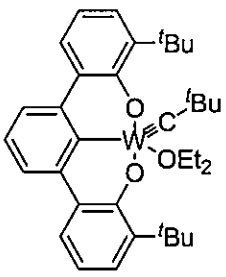
5. The tridentate pincer ligand supported metal complex of claim 1, wherein $XR"_n$ is diethyl ether or tetrahydrofuran.

6. A trianionic pincer ligand supported metal-alkylidyne salt , comprising a tridentate pincer ligand supported metal complex anion and a cation derived from protonation of a base selected from triphenylphosphorane, methylithium, *n*-butyllithium, imidazole, pyrazole, pyridine, and 1,8-diazabicyclo[5.4.0]undec-7-ene.

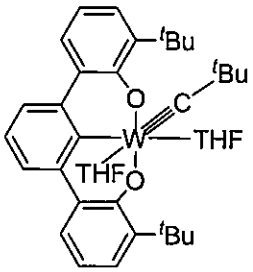
7. The trianionic pincer ligand supported metal-alkylidyne salt of claim 6, having the structure:



8. The tridentate pincer ligand supported metal complex of claim 1, having the structure:

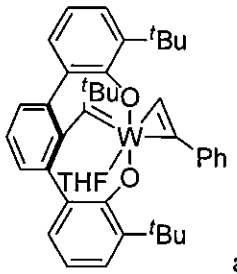


9. The tridentate pincer ligand supported metal complex of claim 1, having the structure:

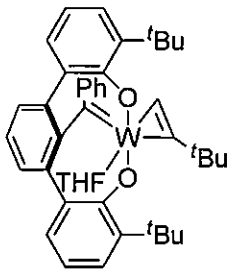


.

10. The tridentate pincer ligand supported metal complex of claim 1, having the structure:

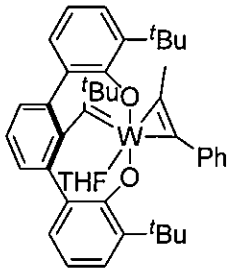


and/or

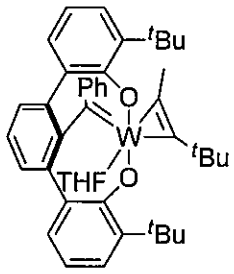


.

11. The tridentate pincer ligand supported metal complex of claim 1, having the structure:

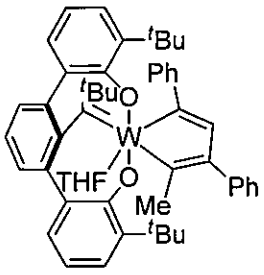


and/or

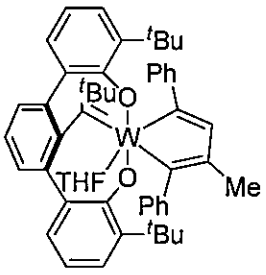


.

12. The tridentate pincer ligand supported metal complex of claim 1, having the structure:

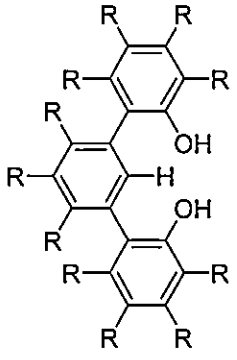


and/or



.

13. A method for the preparation of the tridentate pincer ligand supported metal complex of claim 1, comprising: combining a trialkoxy metal-alkylidyne with an OCO pincer ligand having a 1,1':3',1" terphenyl-2,2"-diol structure:



,

wherein R is independently, H, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, or C_5 to C_{20} alkyl, and wherein the metal of the trialkoxy metal-alkylidyne is a group 5-7 transition metal; and deprotonating the 2'-H of the OCO pincer ligand precursor by addition of a base, wherein the trianionic pincer ligand supported metal-alkylidyne complex of claim 1 is a salt, wherein the anion of the salt is a trianionic pincer ligand supported metal-alkylidyne complex.

14. The method of claim 13, wherein the base is triphenylphosphorane, methyllithium, *n*-butyllithium, imidazole, pyrazole, pyridine, or 1,8-diazabicyclo[5.4.0]undec-7-ene.

15. The method of claim 13, further comprising addition of an electrophile, wherein the salt is converted into a neutral trianionic pincer ligand supported metal-alkylidyne complex.

16. The method of claim 15, wherein the electrophile is an alkyl-triflate or an alkyl-tetrafluoroborate.

17. The method of claim 15, further comprising providing a second ligand and exchanging a first ligand of the neutral trianionic pincer ligand supported metal-alkylidyne complex to form a second neutral trianionic pincer ligand supported metal-alkylidyne complex.

18. The method of claim 17, further comprising adding one to ten equivalents of an alkyne to the second neutral trianionic pincer ligand supported metal-alkylidyne complex to form a tetra-anionic pincer-ligand supported metallacycloalkylene complex.

19. A method of polymerizing an alkyne, comprising: providing a catalytic amount of a tridentate pincer ligand supported metal complex according to claim 1; and combining the trianionic pincer ligand supported metal-alkylidyne complex with a plurality of alkyne monomers to form a poly(alkyne).

20. The method of claim 19, wherein the tridentate pincer ligand supported metal complex and alkyne monomers are provided in an aprotic solvent.

21. The method of claim 19, further comprising providing an electrophile, wherein the tridentate pincer ligand supported metal complex is a salt.

22. The method of claim 19, wherein the poly(alkyne) has a macrocyclic structure.

23. The method of claim 19, wherein the alkyne monomer is phenylacetylene.