

DESCRIPTION

METALLACYCLOALKYLENE COMPLEXES AND USE FOR ALKYNE
POLYMERIZATION TO CYCLIC POLYACETYLENES

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Utility Application Serial No. 14/299,449, filed June 9, 2014, which is a continuation-in-part of International Patent Application No. PCT/US2012/065841, filed November 19, 2012, which claims the benefit of
10 U.S. Provisional Application Serial No. 61/567,909, filed December 7, 2011, and also claims the benefit of U.S. Provisional Application Serial No. 61/845,764, filed July 12, 2013, the disclosures of which are hereby incorporated by reference in their entirety.

This invention was made with government support under CHE-0748408 awarded by
15 the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF INVENTION

High oxidation state alkylidene and alkylidyne metal complexes have been known for about 40 years. Alkene and alkyne metathesis via these metal complexes has been studied
20 extensively. Alkylidyne metal complexes have been studied to a lesser extent than their alkylidene analogues, but they are of particular interest for their potential to promote nitrile-alkyne cross metathesis (NACM), which constitutes a potentially valuable tool to prepare novel alkynes from readily accessible nitriles.

Metal-alkylidynes contain a metal-carbon triple bond. Metal-alkylidynes, having a
25 metal in its highest oxidation state, are known as Schrock-type metal-alkylidynes, and have been widely investigated. In high-oxidation state metal-alkylidynes, the alkylidyne carbon is a 6-electron donor that provides π -donation to the metal center. In spite of extensive π -donation, most high-oxidation state metal-alkylidynes are electron deficient and must be stabilized by additional ligands.

30 Schrock-type metal-alkylidynes are generally formed by the deprotonation of an α -CH, where a base deprotonates the α -carbon to form an alkylidyne from the alkylidene, or by an α -elimination reaction, in which bulky alkyl groups promote deprotonation of the α -CH to release steric crowding during formation of metal-alkylidynes. In rare cases, these complexes

have been formed by a metathesis reaction between an alkyne and a metal-metal triple bond, or by a reductive recycle series of reactions, where a *gem*-dichloride reacts with a metal complex, to form a mixture of a metal chloride complex and a metal alkylidene, followed by reduction of the metal chloride complex back to the original metal complex.

5 A catalytic NACM was reported by Geyer *et al.*, *J. Am. Chem. Soc.* **2007**, *129*, 3800-1, where a tungsten-nitride of the form $(RO)_3W\equiv N$ was found to reversibly convert to the corresponding metal-alkylidyne upon treatment with an alkyne. Unfortunately, rates of reaction were very slow and a very limited substrate scope was observed. Using a novel titanium alkylidene-alkyl complex $(PNP)Ti=CH^tBu(CH_2^tBu)$, where PNP is a phosphorous-
10 nitrogen-phosphorous tridentate pincer-type ligand, and bulky nitriles, NACM was achieved. However, the catalyst required an external electrophile to liberate the alkyne, as reported by Bailey *et al.*, *J. Am. Chem. Soc.* **2007**, *129*, 2234-5.

Polyacetylenes are organic polymers that can display electrical conductivity, paramagnetic susceptibility, optical nonlinearity, photoconductivity, gas permeability, liquid-
15 crystallinity, and chain-helicity. Polymerization of acetylenes employs a transition metal catalyst, generally with a cocatalyst. High molecular weight polyacetylenes ($>10^6$ g/mol) have been produced from catalysts, such as $M(CO)_6-CCl_4-h\nu$ ($M = Mo, W$), where the active species has been determined to be a metal-alkylidene, with polymerization involving a metathesis pathway. The metal-alkylidyne, $(R_3CO)_3W\equiv CC(CH_3)_3$, has been shown to
20 promote alkyne metathesis and alkyne polymerization, as reported by Mortreux *et al.*, *J. Mol. Catal. A: Chem.* **1995**, *96*, 95-105, where the product composition varied with the substitution. Polymerization was shown to be the exclusive path only with phenyl or trimethylsilyl monosubstituted acetylenes. The metal-alkylidyne, $H_5C_6C\equiv W(CO)_4Br$, promotes a slow alkyne polymerization without alkyne metathesis as reported by Katz *et al.*,
25 *J. Am. Chem. Soc.* **1984**, *106*, 2659-68, but only low monomer conversion is observed after periods of days.

One might expect that OCO pincer ligand supported metal-alkylidynes should be well suited as metathesis or polymerization catalysts for alkynes, as: the trianionic nature of the OCO pincer ligand allows access to a +6 oxidation state required for a metal-alkylidyne; the
30 rigid planarity of the OCO pincer ligand imposes geometric restraints around the metal center, which might permit an increase in reactivity; and the strong M-C bond should distort

the metal-alkylidyne out of the plane of the ligand, which might further increase the reactivity of the resulting complex.

The polymerization of monomers into cyclic polymers that do not contain end groups provides polymers that demonstrate unique physical properties. For example, the density, refractive index, T_g , viscoelasticity, solution dynamics, and surface properties of cyclic polymers all differ from those of their more common linear analogs. Despite research in this area for over half a century there still remains a lack of knowledge regarding the properties and fundamental behavior of cyclic analogs of important commercial polymers. Ring closing of large chains is one method of creating cyclic polymers, but requires infinite dilution conditions to be efficient, thus precluding large scale synthesis. Intermolecular cross coupling of two separate chains inevitably leads to linear impurities, where even trace non-cyclic impurities can have pronounced effects on the physical properties of a sample. Exhaustive purification to remove linear byproducts, biphasic conditions, or preparatory scale GPC is often necessary and limits the large scale synthesis of cyclic polymers.

Ring-expansion polymerization is another method for accessing cyclic polymers. The mechanism involves the insertion of monomer into a growing ring at a labile bond, such as a metal-carbon or metal-oxygen bond. Ring expansion method does not suffer the same stringent concentration limitations as ring closure, making it an appealing approach for synthesizing cyclic polymers. A dibutyltin catalyst disclosed in Kricheldorf *Macromolecules* 1995, **28**, 6718-6725, was an early example of this type of polymerization with lactones. In many cases, catalysts must be tuned to specific monomers. Ring-expansion olefin metathesis polymerization (REMP), introduced by Grubbs, and described in Bielawski *et al.*, *Science* 2002, **297**, 2041-2044, and Xia, Y. *et al.*, *J. Am. Chem. Soc.* 2009, **131**, 2670-2677 addresses producing cyclic polymers efficiently. While the ring-expansion method of creating cyclic polymers is much preferred to the post-polymerization processing required in ring-closure for larger scale syntheses, ring-expansion can suffer from backbiting as the degree of polymerization increases and linear polymers can form during the reaction if trace linear alkenes are present in the monomer feedstock.

Additionally, REMP catalyst systems require a cyclic monomer, for example cyclooctene and its derivatives. It would be beneficial to employ more readily available and cheaper substrates. Thus, a longstanding general challenge in polymer chemistry is to

synthesize cyclic polymers efficiently, with diverse compositions, high purity, high molecular weights, and from readily available and inexpensive monomers.

BRIEF SUMMARY

5 An embodiment of the invention is directed to a method for preparation of tetra-anionic pincer-ligand supported metallacycloalkylene complexes from the trianionic pincer ligand supported metal-alkylidyne complexes, according to an embodiment of the invention.

Another embodiment of the invention is directed to the use of the tridentate pincer ligand metal complexes as initiators for the polymerization of alkynes. High molecular
10 weight polymers are formed at high rates using the tridentate pincer ligand metal complexes. In an embodiment of the invention the poly(alkyne) is a macrocyclic poly(alkyne).

Another embodiment of the invention is directed to hydrogenation of the poly-unsaturated cyclic poly(alkyne) to a saturated polymer. A macrocyclic poly(phenylacetylene) can be hydrogenated to cyclic poly(styrene).

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows the synthesis of tetraanionic pincer ligand supported metallacycloalkylene complexes **2**, **3**, and **4**, from trianionic pincer ligand supported metal-alkylidyne complex **1**, according to an embodiment of the invention.

20 FIG 2 shows the X-ray determined molecular structure of **4** with ellipsoids drawn at the 50% probability level and disordered THF atoms and lattice solvent molecule (pentane) removed for clarity with selected bond distances [Å]: W1-O1 1.990(1), W1-O2 1.984(1), W1-O3 2.328(1), W1-C27 2.045(2), W1-C32 2.014(2), W1-C33 1.902(2). Bond Angles [°]: O1-W1-O2 152.37(6), C32-W1-C27 37.47(8).

25 FIG. 3 gives ^1H , and ^{13}C NMR signals for **4**.

FIG. 4 shows plots of TON determined by quantitative yield of poly(phenylacetylene) vs. time (min) for **2**, **3**, and **4**, where averages of data in triplicate are plotted. Shows dynamic light scattering plots of a) cyclic polyphenylacetylene prepared according to an embodiment of the invention, and b) linear polyphenylacetylene of the same molecular weight.

30 FIG. 5A shows GPC traces for cyclic poly(phenylacetylene) according to an embodiment of the invention, and FIG. 5B with matched molecular weight linear.

FIG. 6A shows Dynamic light scattering volume plots for cyclic poly(phenylacetylene) according to an embodiment of the invention, and FIG. 5B with matched molecular weight linear.

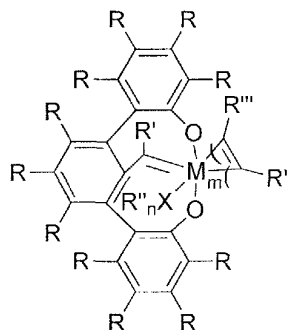
FIG. 7 shows a catalyst loop for the polymerization process carried out by 4.

FIG. 8A shows ozonolysis of cyclic Poly(phenylacetylene) and FIG. 8B for linear poly(phenylacetylene), and samples for 30s and 16 min.

FIG. 9A shows overlaid GPC trace of cyclic and linear PS. With cyclic PS Mw = 31,000, PDI = 1.28; Blue: linear standard PS Mw = 30,000, PDI = 1.06; and FIG. 9B shows overlaid GPC trace of cyclic and linear PS. Black: cyclic PS Mw = 31000, PDI = 1.28; Red: linear standard PS Mw = 20,000, PDI = 1.02.

DETAILED DISCLOSURE

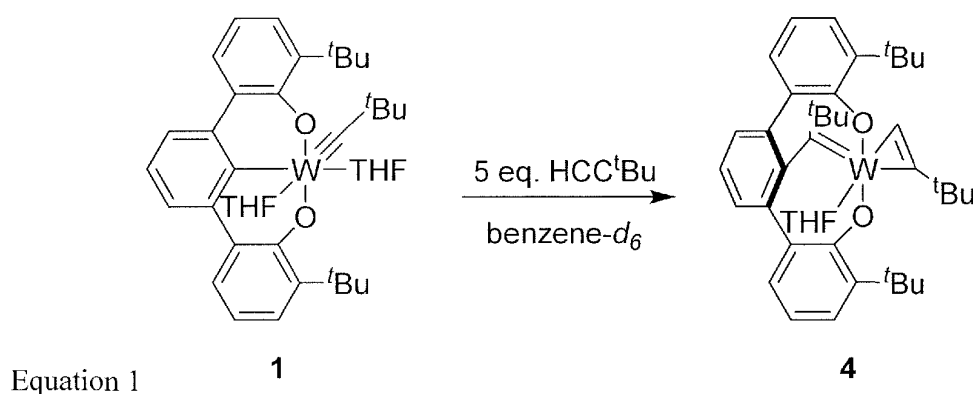
U.S. International Patent Application No. PCT/US2012/065841, filed November 19, 2012 teaches the preparation of trianionic pincer ligand supported metal-alkylidyne complex. It is disclosed therein that upon addition of an alkyne to a trianionic pincer ligand supported metal-alkylidyne complex, conversion occurs into a tetra-anionic pincer-ligand supported metal-alkyne or, as shown below, a tetraanionic pincer ligand supported metallacycloalkylene complex of the structure:



where: R is, independently, H, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, or larger alkyl, or any other substituent that does not inhibit formation of the tetra-anionic pincer-ligand supported metallacycloalkylene; R' is, independently, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, C₅-C₂₂ alkyl, phenyl, naphthyl, C₁₃-C₂₂ aryl, substituted aryl, or trimethylsilyl; R''' is H or methyl; X, independently, is O, N, S, P, or Se; R'', independently, can be methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, C₅-C₂₂, phenyl, naphthyl, C₁₃-C₂₂ aryl, or two R'' are C₄-C₆ alkylene combined with a single X as a heterocycle; n is 1 to 3 depending on X; m is n is 1 to 2; and M is a group 5-7 transition

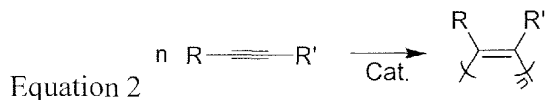
metal. When R' is substituted aryl, one or more substituents can be fluoro, C₁-C₃ alkoxy, or trifluoromethyl.

The tetra-anionic pincer-ligand supported metallacycloalkylene complex is a metallacyclopropylene complex formed by the addition of an alkyne to the trianionic pincer ligand supported metal-alkylidyne complex. As shown in FIG. 1, the preparation of the tetra-anionic pincer-ligand supported metallacycloalkylene complex at low temperature with two equivalents of an acetylene monomer gives a mixture of products toward polymerization. In an embodiment of the invention, multiple equivalents of the acetylene monomer is included with the trianionic pincer ligand supported metal-alkylidyne complex at room temperature results in a single tetra-anionic pincer-ligand supported metallacycloalkylene complex with two like monomers on the resulting tetra-anionic pincer-ligand supported metallacycloalkylene complex, as indicated in Equation 1, below.



An embodiment of the invention is directed to a method for the polymerization of alkynes using a trianionic pincer ligand supported metal-alkylidyne complex or a tetraanionic pincer ligand supported metallacyclopropene complex as the polymerization catalyst. The poly(alkyne)s prepared by this method can display one or more geometries across the resulting double bonds of the poly(alkyne) backbone. The all *cis* alkylene chain, indicated by Equation 2, is for illustrative purposes only, and is not intended to suggest the geometry to be expected upon polymerization of all possible monomers, using all possible trianionic pincer ligand supported metal-alkylidyne complexes, or under any set of reaction conditions. The polymerization reaction occurs upon combining the trianionic pincer ligand supported metal-alkylidyne complex to an alkyne monomer, in a fluid state, which can be in solution. The alkyne can be unsubstituted, monosubstituted, or disubstituted. The trianionic pincer ligand supported metal-alkylidyne complex can be a neutral complex or an anion of a salt when employed with a strong electrophile, such as methyl triflate. The polymerization can be

carried out at relatively mild conditions, for example, ambient temperatures at dry conditions under an inert atmosphere. The polymerization can occur with a large turnover of monomer per catalyst, a high degree of polymerization, and a high yield of polymer. As would be expected by those skilled in the art, the rate of polymerization and the practical conversion varies with the nature of the monomer, catalyst and conditions for the polymerization. In an embodiment of the invention, the resulting poly(alkyne) can be a cyclic polymer.



Complex **4** maintains a high activity that is similar to that observed for catalyst **2**. Loading either catalyst **2**, **3**, or the catalyst **4** in a 10,000:1 phenylacetylene to catalyst ratio in 2 mL of toluene results in polymerization and a product we now understand to be cyclic poly(phenylacetylene). In the first two minutes of polymerization, **2** averages 6.89×10^6 g_{pol}/mol/h, **3** averages 4.39×10^6 g_{pol}/mol/h, but incredibly **4** averages 9.00×10^6 g_{pol}/mol/h. Not only does **4** have excellent activity, it achieves complete conversion under these conditions with a TON $\approx 10,000$ after 22 min. The polymerization carried out in the presence of styrene or excess TEMPO (a radical trap) does not alter or inhibit the polymerization of phenylacetylene. The first indication that the catalysts produce cyclic poly(phenylacetylene) came from the observation that 1-phenyl-1-propyne inserts into the W-alkene bond of **2** to produce a five membered metallacyclopentadiene complex. FIG. 7 shows a scheme for a ring-expansion polymerization of alkynes.

Cyclic polymers have a smaller hydrodynamic volume and thus longer elution time by GPC compared to linear analogs. Also, static and dynamic light scattering techniques can confirm that cyclic polymers have smaller particle radii versus linear equivalents. Calculations indicate the root mean square (rms) radius of gyration ($\langle R_g^2 \rangle^{0.5}$) of a cyclic polymer is half that of the same polymer in a linear topology. In some cases, it is possible to open the resulting macrocycle through bond cleavage, resulting in a linear topology and a subsequent change in physical properties. Linear poly(phenylacetylene) synthesized using (acetylacetonato)(1,5-cyclooctadiene)rhodium(I) as a catalyst offers a comparison to the cyclic polymers produced by **4**, and by matching molecular weights and polydispersities, the effect of topology can be determined unambiguously. Using DLS and SLS techniques, the hydrodynamic radius (R_H) and rms radius of gyration ($\langle R_g^2 \rangle^{0.5}$) were determined for the linear and cyclic polymers. It is well understood that the ratio of $\frac{R_{H \text{ cyclic}}}{R_{H \text{ linear}}} = 0.9$ and

$\frac{\langle R_g^2 \rangle_{\text{cyclic}}}{\langle R_g^2 \rangle_{\text{linear}}} = 0.5$. Table 4, below, lists the experimental values of R_H and R_g for the cyclic and linear polymers. With little doubt the experimentally determined ratios clearly indicate the polymers produced with catalyst **4** are cyclic. The experimental ratios of $\frac{R_H^{\text{cyclic}}}{R_H^{\text{linear}}} = 0.85$ (2) and $\frac{\langle R_g^2 \rangle_{\text{cyclic}}}{\langle R_g^2 \rangle_{\text{linear}}} = 0.35$ (4) clearly indicate a difference in topology. The theoretical values are modeled after polyolefins containing sp^3 linkages, thus deviations from theory are expected for poly(phenylacetylenes) due to the more rigid sp^2 hybridized backbone.

METHODS AND MATERIALS

General Considerations

Unless specified otherwise, all manipulations were performed under an inert atmosphere using glove-box techniques. Toluene and pentane were dried using a GlassCountour drying column. Phenylacetylene was purchased from Sigma-Aldrich, and doubly distilled from calcium hydride, degassed by freeze pump thawing, and filtered through a column of basic alumina immediately prior to use. Toluene- d_8 was dried over phosphorous pentoxide (P_2O_5), distilled, degassed by freeze pump thawing, and stored over 4Å molecular sieves. $[t\text{BuOCO}]W\equiv C(t\text{Bu})(\text{THF})_2$ (**1**) was prepared according to literature procedure. NMR spectra were obtained on Varian INOVA 500 MHz and Varian INOVA2 500 MHz spectrometers. Chemical shifts are reported in δ (ppm). For ^1H and ^{13}C NMR spectra, the residual solvent peaks were used as an internal reference. Molecular weight and polydispersity were determined by size exclusion chromatography (SEC) in dimethylacetamide (DMAc) with 50 mM LiCl at 50 °C and a flow rate of 1.0 mL/min (Agilent isocratic pump, degasser, and auto-sampler, columns: PLgel 5 μm guard + two ViscoGel I-series G3078 mixed bed columns: molecular weight range $0\text{--}20 \times 10^3$ and $0\text{--}100 \times 10^4$ g mol $^{-1}$). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm and a Wyatt miniDAWN Treos light scattering detector operating at 659 nm. Absolute molecular weights and polydispersities were calculated using Wyatt ASTRA software.

Synthesis of $[t\text{BuOCHO}]W\equiv C(\text{CH}_3)_3(\text{O}^t\text{Bu})(\text{THF})$

In a nitrogen filled glove box, a glass vial was charged with $[t\text{BuOCO}]H_3$ (140 mg, 0.37 mmol) in THF (1 mL); and subsequently cooled to -35 °C. In a second vial,

(^tBuO)₃W≡CC(CH₃)₃ (200 mg, 0.42 mmol) was dissolved in THF (1 mL) and the solution was added dropwise to the first solution while stirring. As the solution warmed to room temperature, a gradual color change from brown to dark yellow was observed. Stirring was continued for 30 min at room temperature. A tacky dark yellow material was obtained after removal of volatiles. Cold pentane (4 mL) was added to form a brown suspension, from which a bright yellow precipitate was filtered. The filtrate was washed with additional cold pentane. Single crystals were obtained by cooling a dilute pentane solution at -35 °C for 12 h; yield (206 mg, 72%). ¹H NMR (300 MHz, C₆D₆, δ (ppm)): 8.94 (s, tol-*d*₈, -65 °C, C_{ipso}-H), 7.46 (d, *J* = 7.8 Hz, 4H, Ar-H), 7.33-7.27 (m, 4H, Ar-H), 6.96 (t, *J* = 8.0 Hz, 2H, Ar-H), 3.43 (m, 4H, OCH₂CH₂/THF), 1.67 (s, 18H, -C(CH₃)₃), 1.49 (bs, 9H, -OC(CH₃)₃), 1.29 (m, 4H, OCH₂CH₂/THF), 0.86 (s, 9H, W≡CC(CH₃)₃). ¹³C{¹H}NMR (75.36 MHz, C₆D₆, δ (ppm)): 297.1 (s, W≡CC(CH₃)₃), 165.2 (s, C, aromatic), 144.8 (s, C, aromatic), 138.0 (s, C, aromatic), 130.5 (s, C, aromatic), 127.5 (s, C, aromatic), 126.9 (s, C, aromatic), 121.7 (s, C, aromatic), 80.7 (s, -OC(CH₃)₃), 50.3 (s, W≡CC(CH₃)₃), 35.7 (s, -C(CH₃)₃), 32.9 (s, W≡CC(CH₃)₃), 32.2 (s, -OC(CH₃)₃), 31.3 (s, -C(CH₃)₃). Anal. Calcd for C₃₅H₄₆O₃W: C, 60.18; H, 6.64. Found: C, 59.76; H, 6.74.

Synthesis of {[^tBuOCO]W≡CC(CH₃)₃(O^tBu)}{Ph₃PCH₃}

A glass vial was charged with [^tBuOCHO]W≡C(CH₃)₃(O^tBu)(THF) (206 mg, 0.267 mmol) and Et₂O (1 mL), and subsequently cooled to -35 °C. A solution of Ph₃P=CH₂ (74 mg, 0.267 mmol) in Et₂O (0.5 mL) was prepared and added to the cold solution. The resulting mixture was warmed to 25 °C where the solution changed in color from a “dark” yellow to “canary” yellow. The solution was stirred for 45 min at room temperature, during which time, the salt product precipitated as a yellow solid. The product was filtered, and the filtrate was washed with pentanes (3 x 1 mL) to yield (216 mg, 83%). ¹H NMR (500 MHz, C₆D₆, δ (ppm)): 7.77 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.52 (t, *J* = 7.2 Hz, 4H, Ar-H), 7.04 (d, *J* = 7.3 Hz, 2H, Ar-H), 6.96 (t, *J* = 7.9 Hz, 3H, Ar-H), 6.84 (dt, *J* = 2.5 Hz, *J* = 7.7 Hz, 6H, Ar-H), 6.78 (t, *J* = 7.3 Hz, 1H, Ar-H), 6.58 (d, *J* = 7.9 Hz, 3H, Ar-H), 6.55 (d, *J* = 7.7 Hz, 3H, Ar-H), 2.03 (s, 9H, -OC(CH₃)₃), 1.97 (s, 18H, -C(CH₃)₃), 1.83 (d, *J*_{PH} = 12.8 Hz, 3H, P-CH₃), 0.91 (s, 9H, W≡CC(CH₃)₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, δ (ppm)): 305.3 (s, W≡CC(CH₃)₃), 205.3 (s, W-C_{pincer}), 164.8 (s, C, aromatic), 143.1 (s, C, aromatic), 137.2, 135.2 (d, *J*_{CP} = 2.7 Hz, C, aromatic), 133.1 (d, *J*_{CP} = 10.1 Hz, C, aromatic), 130.7 (d, *J*_{CP} = 12.8 Hz, C, aromatic), 127.9 (s, C, aromatic), 124.7 (s, C, aromatic), 124.4 (s, C, aromatic), 124.0 (s,

C, aromatic), 119.6 (s, C, aromatic), 118.5 (d, $J_{CP} = 7.3$ Hz, C, aromatic), 76.2 (s, -OC(CH₃)₃), 50.2 (s, W≡CC(CH₃)₃), 36.5 (s, -C(CH₃)₃), 34.9 (-OC(CH₃)₃), 34.0 (s, W≡CC(CH₃)₃), 31.8 (s, -C(CH₃)₃), 9.1 (d, $J_{CP} = 56.7$ Hz). ³¹P{¹H} NMR (121 MHz, C₆D₆, δ (ppm)): 21.6. Anal. Calcd for C₅₄H₆₃O₃PW: C, 66.53; H, 6.51. Found: C, 66.57, H, 6.51.

5 Attempts to obtain single crystals of the complex were unsuccessful. The combination of ¹H, ¹³C, ³¹P, and correlation experiments using NMR spectroscopy and combustion analysis allowed for unambiguous identification.

Synthesis of [^tBuOCO]W≡CC(CH₃)₃(THF)₂ (1)

A glass vial was charged with {[^tBuOCO]W≡CC(CH₃)₃(O^tBu)} {Ph₃PCH₃} (115 mg, 10 0.164 mmol) and Et₂O (5 mL) to provide an orange suspension. THF (0.1 mL) was added to precipitate phosphoniumtriflate as a white solid. The solution was filtered and concentrated under reduced pressure. Cooling the solution to -35 °C for 12 h yielded compound **1** as a “dark” red crystalline material; yield (100 mg, 78%). ¹H NMR (500 MHz, C₆D₆, δ (ppm)): 8.00 (d, $J = 7.4$ Hz, 2H, Ar-*H*), 7.84 (d, $J = 8.5$ Hz, 2H, Ar-*H*), 7.46 (d, $J = 7.9$ Hz, 2H, Ar-*H*), 7.35 (t, $J = 8.5$ Hz, 1H, Ar-*H*), 7.05 (t, $J = 7.5$ Hz, 2H, Ar-*H*), 4.07 (br, 4H, OCH₂CH₂/THF), 3.40 (br, 4H, CH₂CH₂/THF), 1.65 (s, 18H, -C(CH₃)₃), 1.45 (br, 4H, OCH₂CH₂/THF), 1.16 (br, 4H, OCH₂CH₂/THF), 0.61 (s, 9H, W≡CC(CH₃)₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, δ (ppm)): 320.7 (s, W≡CC(CH₃)₃), 193.5 (s, W-C_{ipso}), 163.1 (s, C, aromatic), 139.2 (s, C, aromatic), 135.4 (s, C, aromatic), 134.5 (s, C, aromatic), 128.0 (s, C, aromatic), 126.4 (s, C, aromatic), 125.3 (s, C, aromatic), 124.3 (s, C, aromatic), 119.9 (s, C, aromatic), 76.8 (s, OCH₂CH₂/THF), 67.3 (s, OCH₂CH₂/THF), 48.6 (s, W≡CC(CH₃)₃), 35.3 (s, -C(CH₃)₃), 32.5 (s, W≡CC(CH₃)₃), 30.6 (s, -C(CH₃)₃), 25.6 (s, OCH₂CH₂/THF), 24.9 (s, OCH₂CH₂/THF). Anal. Calcd for C₃₉H₅₂O₄: C, 60.94; H, 6.82. Found: C, 60.88, H, 6.87.

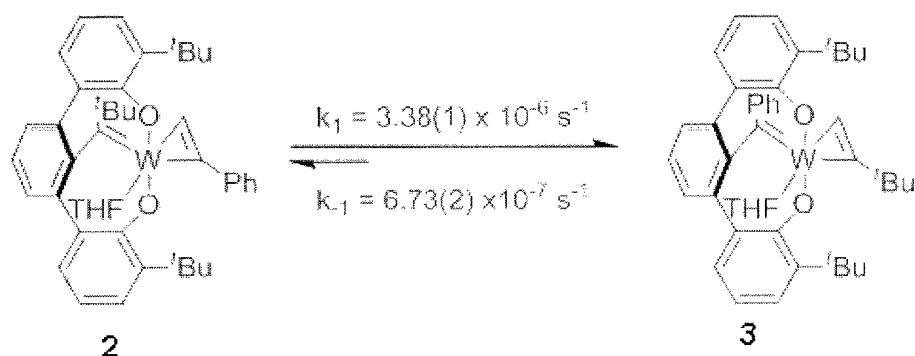
A combination of ¹H and ¹³C NMR spectroscopy with combustion analysis allowed 25 the unambiguous identification of **1**. X-Ray Intensity data were collected at 100 K on a Bruker DUO diffractometer using MoK α radiation ($\lambda = 0.71073$ Å) and an APEXII CCD area detector. Raw data frames were analyzed by the program SAINT and integrated using 3D profiling algorithms. Reducing the resulting data produced the hkl reflections and their corresponding intensities and estimated standard deviations. The data were corrected for 30 Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

Synthesis of $[\text{O}_2\text{C}(\text{tBuC=})\text{W}(\eta^2\text{-HC}\equiv\text{CPh})]$ (2**) and $[\text{O}_2\text{C}(\text{PhC=})\text{W}(\eta^2\text{-HC}\equiv\text{CtBu})]$ (**3**)**

Complex **1** reacts instantaneously with 2 equiv. of phenylacetylene in toluene- d_8 at -35 °C to yield $[\text{O}_2\text{C}(\text{tBuC=})\text{W}(\eta^2\text{-HC}\equiv\text{CPh})]$ (**2**) and $[\text{O}_2\text{C}(\text{PhC=})\text{W}(\eta^2\text{-HC}\equiv\text{CtBu})]$ (**3**) in a 2:1 ratio, along with small amounts of polyphenylacetylene (PPA) (Scheme 1). Adding Et_2O to the mixture of compounds selectively dissolves the two complexes, and filtering results in the separation of Et_2O -insoluble PPA. Adding pentane to the mixture of **2** and **3** selectively dissolves **2**, and filtering results in the segregation of **3**, a pentane-insoluble orange solid in 33% yield. The pentane soluble solution of **2** was reduced under vacuum to yield a yellow solid in 40% yield.

Single crystals amenable to an X-ray diffraction experiment deposit from a concentrated solution of **3** in Et_2O at -35 °C. **3** and **2** feature the unusual combination of a tridentate tetra-anionic pincer-type ligand comprising two phenolate and an alkylidene connection.

Complexes **2** and **3** form in a 2 to 1 ratio from **1** and phenylacetylene at -35 °C. As illustrated in equation I, below, heating a solution of isolated **2** in toluene- d_8 at 85 °C for 2.5 weeks established **2** and **3** in equilibrium. At equilibrium, integration of the respective protons on the $\eta^2\text{-HC}\equiv\text{CPh}$ and $\eta^2\text{-HC}\equiv\text{CtBu}$ moieties indicates that **2** and **3** exist in a 17:83 ratio ($K_{\text{eq}} = 5$), corresponding to an energy difference of -1.14 kcal/mol at 85 °C.



Equation I

Polymerization of Alkynes

In a nitrogen filled glove-box a stock solution of $[\text{tBuOCO}]\text{W}=\text{CC}(\text{CH}_3)_3(\text{THF})_2$ (**1**) (0.2 μmol in 50 μL toluene) was added to anhydrous monomer dissolved in toluene (1000 μmol). The mixture was allowed to stir at room temperature for 30 minutes. The reaction mixture was removed from the glove-box and precipitated in either methanol or diethyl ether

(20 mL). The polymeric material was collected by filtration and dried under vacuum at 80 °C for 2 hours prior to weighing to obtain the yield

Complex **1** catalyzes phenylacetylene polymerization, complexes **2** and **3** also catalyze phenylacetylene polymerization, suggesting that **1** converts to **2** and **3** in the presence of phenylacetylene.

In a typical reaction, a toluene solution of the catalyst was added to the stirring solution of acetylene monomer and toluene. The reaction was vigorously stirred for 1 h and quenched with methanol. The resulting polymer was dried in vacuo and weighed to provide the quantitative percent yield and turnover number (TON). Polymer characterization includes FTIR and ¹H NMR as well as gel permeation chromatography (GPC) for all samples soluble in THF to determine M_w and M_w/M_n. Polymerization results using **1** are given in Table 1, below.

Table 1 Acetylene polymerization results using **1**^[a]

Monomer	% Yield	TON	M _w ^[b]	M _w /M _n ^[b]
1-ethynyl-4-methoxybenzene	91	4540	39056	2.24
Phenylacetylene	99	4994	33692	3.17
1-ethynyl-4-fluorobenzene	70	3497	34980	3.16
1-ethynyl-3,5-bis(trifluoro-methyl) benzene	10	525	10980	1.46
1-decyne	96	4810	165915	1.27
3,3-dimethyl-1-butyne ^[c]	95	950	3235	1.56
trimethylsilylacetylene ^{[c][d]}	66	672	-	-

^[a]**1** (0.2 μmol) in toluene was added to acetylene monomer (1000 μmol) in toluene for 1 h at 25 °C. ^[b]Determined by GPC. ^[c]**1** (1.0 μmol) in toluene was added to acetylene monomer (1000 μmol) in toluene and heated for 1 h at 75 °C. ^[d]M_w and M_w/M_n could not be determined due to polymer insolubility in THF.

A most remarkable feature of the catalysis is the exceptionally high activity and turnover number. Complexes **1**, **2** and **3** were screened to find the highest attainable turnover number and catalytic activity. Complex **2** supplies the best catalytic values in all cases. With a substrate-to-catalyst loading of 25,000 to 1, complex **2** turns over approximately 17,233 phenylacetylene monomer units, as indicated in Table 2, below. Additionally, **2** polymerizes phenylacetylene and 1-decyne with catalytic activities up to 5.64 x 10⁶ g_{PPA} mol⁻¹ h⁻¹ and 7.98 x 10⁶ g_{PA} mol⁻¹ h⁻¹, respectively.

Table 2 Optimized polymerization results using **2**

Monomer	mon:cat	% Yield	t (min)	TON	g _{PA} /mol/h
Phenylacetylene	25,000 : 1	69	60	17,233	1,760,000
Phenylacetylene	10,000 : 1	92	10	9,204	5,640,000
1-Decyne	10,000 : 1	96	10	9,620	7,980,000

Synthesis of Catalyst [O₂C(*i*BuC=)W(η^2 -HC $\equiv$ C*i*Bu)] **4**

In a nitrogen filled glovebox, a glass vial equipped with a stir bar was charged with **1** (400 mg, 0.52 mmol) and dissolved in toluene (5.0 mL). 3,3-dimethyl-1-butyne (214 mg, 321 μ L, 2.60 mmol) was added via micropipette with stirring. After 5 min, the solvent and residual 3,3-dimethyl-1-butyne were removed in vacuo to yield the light brown solid **4** in >99% yield (405 mg, 0.52 mmol), for the reaction indicated in Equation 2, above. The resulting solid was dissolved in minimal pentane and cooled to -35 °C to yield single crystals amenable to X-ray diffraction, where the molecular structure is shown in FIG. 2. ¹H NMR (500 MHz, C₇D₈, δ (ppm)): 11.61 (s, 1H, W-CH₃₂), 7.41 (d, 2H, Ar-H_{8,10}), 7.28 (dd, 2H, Ar-H_{3,16}), 7.26 (t, 1H, Ar-H₉), 7.19 (dd, 2H, Ar-H_{5,14}), 6.77 (t, 2H, Ar-H_{4,15}), 3.60 (t, 4H, THF-H_{38,41}), 1.66 (s, 9H, W-C-C(CH₃)₃ (H₂₉₋₃₁)), 1.20 (s, 18H, ligand C(CH₃)₃ (H_{20-22,24-26})), 1.16 (t, 4H, THF-H_{39,40}), 0.90 (s, 9H, W=C(CH₃)₃ (H₃₅₋₃₇)). ¹³C NMR: 268.8 (s, W=CC(CH₃)₃ (C₃₃)), 213.0 (s, WCCC(CH₃)₃ (C₂₇)), 184.0 (s, WCCC(CH₃)₃ (C₃₂)), 168.5 (s, C_{1,18}), 153.7 (s, Ar-C_{7,11}), 137.4 (s, Ar-C_{6,13}), 137.3 (s, Ar-C_{2,17}), 132.5 (s, Ar-C₁₂), 130.9 (s, Ar-C₉), 129.2 (s, Ar-C_{8,10}), 128.2 (s, Ar-C_{3,16}), 125.7 (s, Ar-C_{5,14}), 118.7 (s, Ar-C_{4,15}), 71.3 (s, THF-C_{38,41}), 46.0 (s, W=CC(CH₃)₃ (C₃₄)), 39.2 (s, WCCC(CH₃)₃ (C₂₈)), 36.0 (s, W=CC(CH₃)₃ (C₃₅₋₃₇)), 34.3 (s, ligand C(CH₃)₃ (C_{19,23})), 31.1 (s, WCCC(CH₃)₃ (C₂₉₋₃₁)), 30.1 (s, ligand C(CH₃)₃ (C_{20-22,24-26})), 25.00 (s, THF C_{39,40}). Anal. Calcd.: C: 63.24% H: 6.99%, Found: C: 63.28%, H: 7.09%. FIG. 3 gives the structure of **4** with tabulation of the ¹H and ¹³C chemical shifts.

Polymerization Procedure using **4**

In an inert atmosphere glove box, toluene (2.0 mL) was added to a glass vial equipped with a stir bar. Phenylacetylene (218 μ L, 2.00 mmol) was added via micropipette with stirring. A stock solution (1 mg/mL) of **4** (157 μ L, 0.20 μ mol) was added to the stirring solution in one shot to initiate polymerization. Polymerization was terminated via addition into tenfold excess of stirring methanol. Turnover number with time are given for catalysts **1**, **2**, and **3** are shown in FIG. 4A, and for **2**, **3**, and **4** in FIG. 4B. The resulting polymer samples were isolated via vacuum filtration and residual solvent removed in vacuo. Table 3 and Table 4 give kinetic data as yield per polymerization duration for three trials where the GPC and

dynamic light scattering plots are shown in FIGs 5A and 6A, respectively, for cyclic polymer from **4** with FIGs. 5B and 6B display the linear equivalents, respectively. Rudimentary kinetic data and the tabulated hydrodynamic volume dependent characterization data is provided in Tables 3 and 4, below.

Table 3 Triplicate polymerization of phenylacetylene by **4**.

	Trial 1	Trial 2	Trial 3	
Time (s)	Yield (mg)	Yield (mg)	Yield (mg)	Average
30	50	34	67	50.3
150	77	73	75	75.0
300	98	93	90	93.7
600	111	133	104	116.0
900	134	146	168	149.3

Table 4 M_n , M_w/M_n , R_H , and $(\langle R_g^2 \rangle^{0.5})$ values for linear and cyclic poly(phenylacetylene).

Catalyst	M_n (absolute)	M_w/M_n	Radius (R_H)	Radius ($\langle R_g^2 \rangle^{0.5}$)
4 (cyclic)	68,000 Da	1.77	8.4(1) nm	11.7(1.8) nm
(COD)Rh ^I (acac) (linear)	70,000 Da	1.83	9.8(2) nm	19.8(1.0) nm

General Hydrogenation Procedure

Hydrogenation was performed using a 150 mL Parr high-pressure stainless steel reaction vessel equipped with a 50 mL glass round bottom flask and a Teflon stirring bar. Unsaturated polymers were dissolved in anhydrous toluene and degassed for 1 h before adding Pd/C. The round bottom flask was placed into the reactor and then sealed. The Parr vessel was purged with 500 psi of H₂ three times. The pressure reactor was then charged to the desired psi, and the mixture was stirred. Pd/C added every two days in the process. The resultant polymer was filtered through Celite® and precipitated into cold methanol to obtain a solid, which was then filtered and transferred to a vial and dried under high vacuum (3×10^{-4} mmHg) overnight. Different hydrogenation conditions are shown in supplementary Table 5. Entry 1, 2, 3 are the conditions of partial hydrogenations and entry 4 is full hydrogenation conditions.

Table 5 Catalytic hydrogenation via Pd/C

Entry	Loading (wt%)	Temperature (°C)	Time (days)	psi	Color
1	10	75	2	750	yellow
2	10,10	75	4	900	Light yellow
3	15,15	90	5	900	Trace color
4	15,15,15	90	6	900	white

The cyclic and linear poly(phenylacetylene) samples were partially hydrogenated (saturated) using palladium on carbon. The partial hydrogenation enables the ring to be cleaved via ozonolysis. Subjecting a partially hydrogenated sample of linear poly(phenylacetylene) to ozonolysis will only result in C=C bond cleavage to provide fragments with smaller hydrodynamic volumes, and consequently lower molecular weights. It is impossible to create polymers with larger hydrodynamic volumes upon cleavage of a linear polymer. However, cleavage of a cyclic polymer will result in a linear fragment that will have a larger hydrodynamic volume, thus a shorter elution time on a GPC column. FIG. 8 shows GPC traces of polymer fragments from ozonolysis of cyclic poly(phenylacetylene) FIG. 8A and linear FIG. 8B. As evident from the shoulder at 14 min, ozonolysis leads to a fraction of polymers exhibiting shorter elution times, a result only possible if the polymer was cyclic. Since the hydrogenation is not selective, there is a growth in higher elution time fragments as well, as rings with multiple double bonds are opened and then cleaved into smaller and smaller fragments. By comparison, in b, ozonolysis of linear poly(phenylacetylene) produces only smaller fragments with longer elution times. Dynamic light scattering provides an alternative experimental verification of the cyclic topology. The average hydrodynamic radius of the hydrogenated cyclic polymer before ozonolysis is 10.14 nm; however, after ozonolysis the average hydrodynamic radius increases to 12.49 nm, a result only possible for a cyclic polymer.

The hydrogenated polymers display the cyclic nature of the polymers produced from catalyst **4**. By fully hydrogenating cyclic poly(phenylacetylene) cyclic polystyrene is obtained. The cyclic polystyrene are compared with authentic and well characterized linear polystyrene standards. FIG. 9A shows GPC traces of cyclic polystyrene ($M_n = 31,000$; PDI = 1.28) with closely matched linear polystyrene ($M_n = 30,000$; PDI = 1.06). The two samples exhibit significantly different retention times despite having nearly identical absolute molecular weights. Moreover, in an attempt to match elution times, FIG. 9B displays

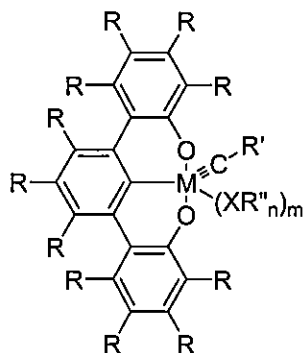
overlapping GPC traces of cyclic polystyrene ($M_n = 31,000$; $PDI = 1.28$) with dramatically smaller linear polystyrene ($M_n = 20,000$; $PDI = 1.02$).

5 All publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

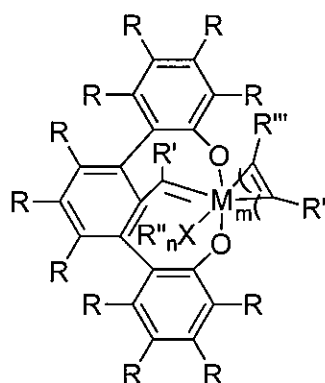
It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application.

CLAIMS

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

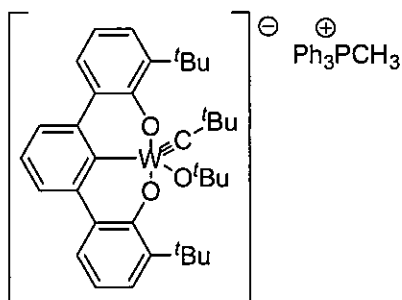


where: M is a group 5-7 transition metal; R is independently, H, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, or C₅ to C₂₀ alkyl; R' is methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, C₅ to C₂₀ alkyl, phenyl, naphthyl, or C₁₃ to C₂₂ aryl; X is independently 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, C₅ to C₂₀ alkyl, phenyl, naphthyl, C₁₃ to C₁₈ aryl or two R'' are combined as a C₄ to C₆ alkylene, wherein XR''₂ is a 5 to 7-membered ring; or

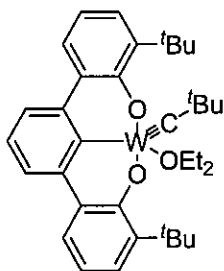


where: R is, independently, H, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, or larger alkyl; R' is, independently, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, C₅-C₂₂ alkyl, phenyl, naphthyl, C₁₃-C₂₂ aryl, aryl substituted with one or more fluoro, C₁-C₃ 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, C₅-C₂₂, phenyl, naphthyl, C₁₃-C₂₂ aryl, or two R'' are combined as a C₄ to C₆ alkylene; n is 1 to 3 depending on X; m is 1 to 2; and M is a group 5-7 transition metal.

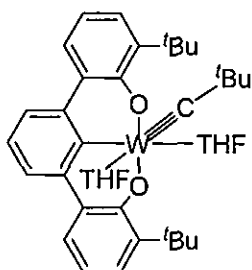
2. The tridentate pincer ligand supported metal complex of claim 1, wherein M is W.
3. The tridentate pincer ligand supported metal complex of claim 1, wherein R is alkyl in the 3 and 3'' positions and H in all other positions.
4. The tridentate pincer ligand supported metal complex of claim 1, wherein 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:



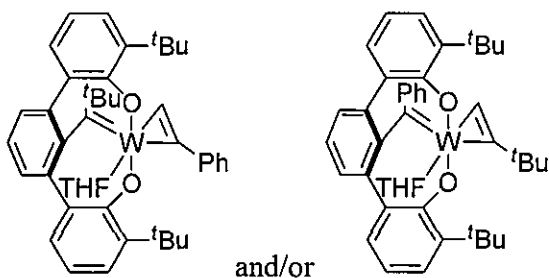
8. The tridentate pincer ligand supported metal complex of claim 1, having the structure:



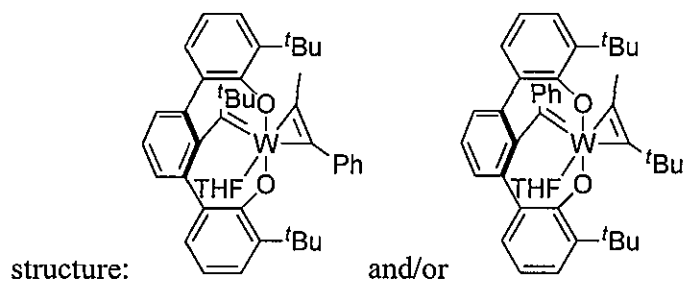
9. The tridentate pincer ligand supported metal complex of claim 1, having the structure:



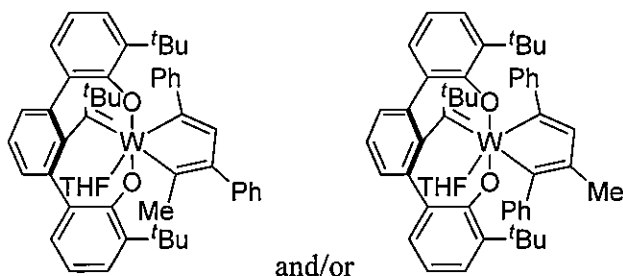
10. The tridentate pincer ligand supported metal complex of claim 1, having the structure:



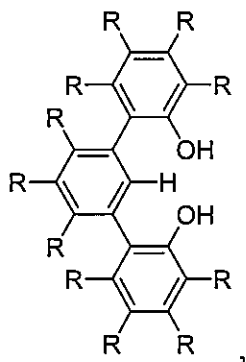
11. The tridentate pincer ligand supported metal complex of claim 1, having the



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



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 C₅ to C₂₀ 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.