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Communication

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An OCO^{3-} Trianionic Pincer Tungsten(VI) Alkylidyne: Rational Design of a Highly Active Alkyne Polymerization Catalyst

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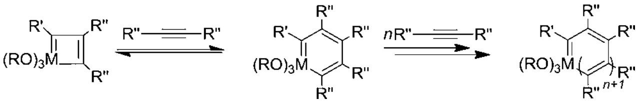
Supporting Information

ABSTRACT: Synthesis, characterization, and catalytic alkyne polymerization results for the first trianionic pincer alkylidyne complex, $[^t\text{BuOCO}]\text{W}{\equiv}\text{CC}(\text{CH}_3)_3(\text{THF})_2$ (**6**), are described. Complex **6** is a highly active catalyst for the polymerization of acetylenes and exhibits a high turnover number (4371), activity (1.05×10^6 g_{PPA} $\text{mol}_{\text{cat}}^{-1}$ h^{-1}), and yield (87%) for the polymerization of 1-ethynyl-4-fluorobenzene.

Isolable high-oxidation-state alkylidyne complexes continue to receive significant attention for applications in catalysis,[1] especially now that some are commercially available and synthetic protocols are established for easily accessible versions.[2] One application is the polymerization of unsaturated substrates. Polyacetylenes (PAs) and polyphenylacetylenes (PPA) are an important class of functional materials that possess unique properties, including electrical conductivity, paramagnetic susceptibility, optical nonlinearity, photoconductivity, gas permeability, liquid crystallinity, and chain helicity.[3] Catalysts containing a metal–alkyl bond polymerize alkynes via an insertion mechanism.[3a−d] Alternatively, transition-metal alkylidenes[4] and metal halide multicomponent catalysts that form a M═C bond in situ[3c] operate via a metathesis mechanism, including examples capable of living polymerization.[5]

Alkylidyne complexes also polymerize alkynes via metathesis[6] and insertion[7] mechanisms. One proposed insertion pathway involves ring expansion (Scheme 1).[7d,8] Initial alkylidyne–alkyne cycloaddition provides the prototypical metallacyclobutadiene intermediate. Next, a *second* acetylene monomer coordinates and inserts to expand the ring.[9] The subsequent steps involve similar ring expansion to generate larger MC_x rings (x odd) with alternating single and double bonds.[7b,d] Schrock and co-workers proposed an alternative ring expansion step via an associative mechanism for catalysts bearing smaller fluorinated alkoxides.[10] Also, deprotonation of the metallocyclobutadiene intermediate or protonation of the alkylidyne can lead to alkylidene species that are active alkyne polymerization catalysts.[11] Each mechanism shares a common feature: a second substrate must bind to a metallocyclobutadiene intermediate. Thus, ligands capable of forcing open or labile metal coordination sites should promote alkyne polymerization.

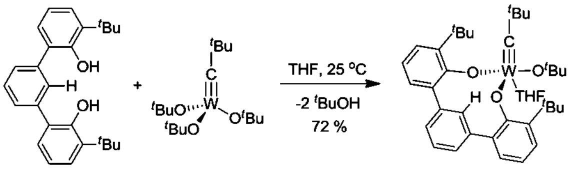
Scheme 1. Proposed Ring Expansion Polymerization of Alkynes



Trianionic pincer ligands[12] constrain three anionic donors to a meridional plane and are capable of supporting high-oxidation-state metal complexes with vacant coordination sites and M–X multiple bonds (X = N, O, C).[13] Thus, coordination of a second alkyne to a metallacyclobutadiene intermediate bearing a trianionic pincer should be feasible (Figure 1). Building on initial progress in synthesizing trianionic pincer alkylidene complexes,[13e] we now describe the synthesis of the first OCO^{3-} trianionic pincer alkylidyne and its catalytic application in PPA synthesis.

Figure 1. Illustration of how trianionic pincer ligands can facilitate coordination of a second alkyne.

Alcoholysis between 1 equiv of $(^t\text{BuO})_3\text{W}{\equiv}\text{C}^t\text{Bu}$ (**2**) and terphenyl diol **1** (denoted as $[^t\text{BuOCO}]\text{H}_3$) in THF affords $[^t\text{BuOCHO}]\text{W}{\equiv}\text{CC}(\text{CH}_3)_3(\text{O}^t\text{Bu})(\text{THF})$ (**3**) as a yellow crystalline solid in 72% yield (eq 1). Figure 2 depicts the structure of **3** determined by single-crystal X-ray diffraction (XRD). The pincer ligand binds to the metal ion in the diphenolate form, creating a five-coordinate W(VI) ion in a distorted trigonal-bipyramidal (tbp) geometry with an Addison parameter $\tau = 0.85$.[14]



(1)

1 **2** **3**

The pincer ligand chelates through the phenolate donors in the tbp equatorial sites, creating a large O1–W1–O2 angle of 135.65(9)°. A $^t\text{BuO}^-$ ligand occupies the remaining equatorial

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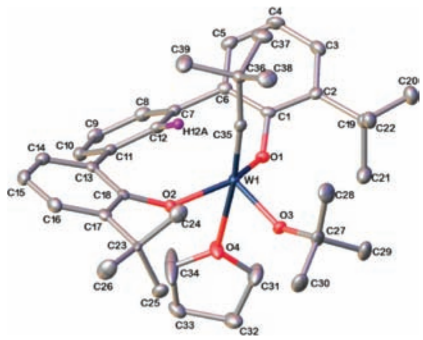
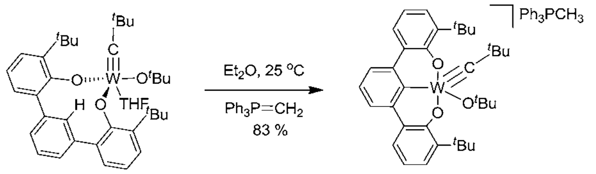


Figure 2. Structure of [^{t}BuOCHO]W≡CC(CH$_3$)$_3$(O^{t}Bu) (THF) (**3**).

coordination site with correspondingly smaller angles [O3−W1−O2 = 103.51(8)° and O3−W1−O1 = 104.21(9)°]. THF and the alkylidyne fragment occupy axial sites with a near-linear C35−W1−O4 bond angle of 173.30(1)° and a W1−C35 bond length of 1.773(4) Å. To the best of our knowledge, the W1−O4 bond length of 2.458(3) Å is the longest reported for a THF coordinated to W(VI); such bond elongation is attributable to the trans influence of the tungsten−alkylidyne. The longest crystallographically characterized W−THF bond found for W(IV) [2.571(3) Å] is in the paddlewheel complex W$_2$(μ_2-O$_2$CAr)$_4$(THF)$_2$ [Ar = *p*-(OMe)C$_6$H$_4$].[15] Presumably, the W−W quadruple bond imparts an even stronger trans influence on the W−THF bond.

In solution, complex **3** exhibits a ^{1}H NMR spectrum indicative of C_s symmetry. Three singlets attributable to the ^{t}Bu protons of the pincer, the *tert*-butoxide, and the alkylidyne appear at 1.67, 1.49, and 0.86 ppm, respectively. Consistent with documented examples of metal complexes bearing a diphenolate, the C$_{ipso}$−H appears downfield at 8.74 ppm (toluene-d_8, −65 °C).[12a,16] The most salient feature in the ^{13}C{^{1}H} NMR spectrum is a resonance at 291.7 ppm for the alkylidyne carbon.

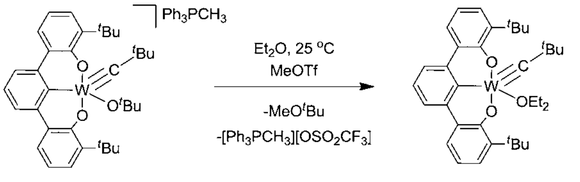
Treating **3** with methylene(triphenyl)phosphorane (Ph$_3$P=CH$_2$) in Et$_2$O at 25 °C precipitates the analytically pure trianionic pincer alkylidyne salt {[^{t}BuOCO]W≡CC(CH$_3$)$_3$(O^{t}Bu)}{PPh$_3$CH$_3$} (**4**) as a canary-yellow microcrystalline solid in 83% yield (eq 2). Complex **4** is the first



3 **4** (2)

trianionic-pincer-supported metal alkylidyne.[17] A combination of ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR and combustion analyses permits the unambiguous assignment of **4** [see the Supporting Information (SI)]. A distinct singlet at 1.97 ppm for the 18 ^{t}Bu protons of the OCO^{3-} ligand indicates that **4** is C_s-symmetric in solution. The mirror plane bisects the terphenyl pincer and contains all three W−C$_{pincer}$, W−O^{t}Bu, and W≡CC(CH$_3$)$_3$ bonds. The ^{t}Bu protons of the alkylidyne appear upfield at 0.91 ppm, and the ^{t}Bu protons of the alkoxide appear as a broad signal at 2.03 ppm. A doublet at 1.83 ppm (J_{P-H} = 12.8 Hz) corresponds to the methyl protons in the phosphonium cation. Two distinct resonances in the ^{13}C{^{1}H} NMR spectrum at 305.3 and 205.3 ppm correspond to the W≡CC(CH$_3$)$_3$ carbon and the W−C$_{pincer}$ carbon, respectively. Consistent with documented examples such as {[^{t}BuOCO]Mo=CHC(CH$_3$)$_2$Ph(NAr)}{Ph$_3$PCH$_3$}[18] and {Mo≡CC(CH$_3$)$_3$(NAr)(OCCH$_3$(CF$_3$)$_2$)$_2$}{Ph$_3$PCH$_3$},[19] the ^{31}P{^{1}H} NMR spectrum of **4** reveals a singlet at 21.6 ppm for the phosphonium countercation.

Treating **4** with methyl triflate in Et$_2$O results in O-alkylation of the alkoxide, providing the coordinatively unsaturated *neutral* trianionic pincer alkylidyne [^{t}BuOCO]W≡CC(CH$_3$)$_3$(Et$_2$O) (**5**) as a red-orange solid (eq 3). Phosphonium triflate ([Ph$_3$PCH$_3$][OSO$_2$CF$_3$]) formed during the alkylation partially precipitated as a white solid but could not be completely removed. The ^{1}H NMR spectrum of the bulk material reveals resonances associated with **5** and a doublet at 1.85 ppm (J_{P-H} = 12.8 Hz) attributable to the methyl protons of residual phosphonium triflate. Resonances consistent with C_s-symmetric **5** appear at 0.67 and 1.95 ppm for the alkylidyne and ^{t}Bu protons of the ligand, respectively. Signals for the coordinated diethyl ether appear at 1.12 and 3.27 ppm.



4 **5** (3)

Single crystals amenable for XRD interrogation deposit from a concentrated Et$_2$O solution of **5** at −35 °C. Figure 3 depicts the solid-state molecular structure of **5**, in which the trianionic pincer ligand is bound to the W(VI) ion in a tridentate meridional fashion. The W(VI) ion is in a square-pyramidal geometry with a calculated Addison parameter τ = 0.14.[14] The W(VI) ion resides 0.49 Å above the O1−O3−O2−C12 basal plane. The W−C$_{pincer}$ bond length of 2.134(5) Å is normal compared to other trianionic pincer tungsten complexes.[13e] The coordinated Et$_2$O is rather weakly bound to the metal, as evidenced by the long W1−O3 bond of 2.185(2) Å. The most comparable complex is W(OAr)$_4$Cl(Et$_2$O)[20] (Ar = 2,6-Cl$_2$C$_6$H$_3$), with a W(V)−OEt$_2$ bond length of 2.104(13) Å. Mimicking the OCO arrangement of the donor ligands, the closely related bisaryloxide alkyl complex (ArO)$_2$(CH$_3$)$_3$CCH$_2$W≡CC(CH$_3$)$_3$ contains a W(VI)≡C bond length of 1.755(2) Å,[2e] which is only slightly longer than the W1−C27 bond length of 1.743(3) Å in **5**.

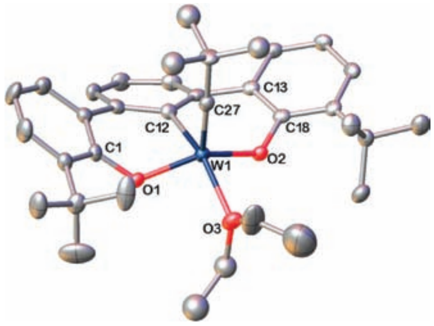
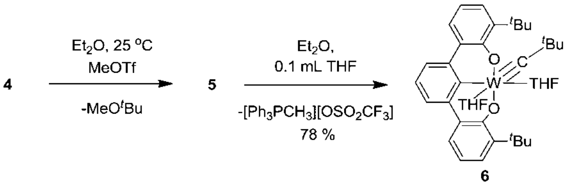


Figure 3. Structure of [^{t}BuOCO]W≡CC(CH$_3$)$_3$(Et$_2$O) (**5**).

Employing a modified route provides analytically pure phosphonium triflate-free alkylidyne (eq 4). Addition of 0.1



(4)

mL of THF to an ether suspension of **5** and $[Ph_3PCH_3]$-$[OSO_2CF_3]$ selectively dissolves the tungsten complex over the salt. Subsequent filtration to remove $[Ph_3PCH_3][OSO_2CF_3]$ and cooling of the filtrate to −35 °C overnight provides analytically pure dark-red single crystals of $[^tBuOCO]W{\equiv}CC(CH_3)_3(THF)_2$ (**6**).

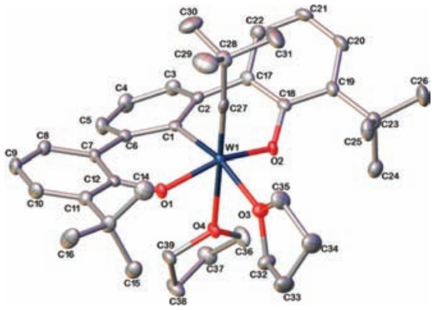
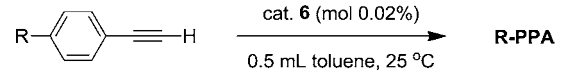


Figure 4. Structure of $[^tBuOCO]W{\equiv}CC(CH_3)_3(THF)_2$ (**6**).

A combination of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, single-crystal XRD, and combustion analysis permits the unambiguous identification of **6**. Figure 4 depicts the solid-state molecular structure of **6**. Unlike **5**, the W ion now binds two THF molecules with W1−O4 and W1−O3 bond lengths of 2.473(2) and 2.177(2) Å, respectively. Appropriately, the different bond lengths suggest that the alkylidyne ligand imparts a stronger trans influence than the aryl $M{-}C_{pincer}$ bond. The pincer ligand is clearly bound in its trianionic form, and the pincer phenoxide donors span an angle of 153.47(10)°. The $W1{-}C_{pincer}$ bond length of 2.132(3) Å is statistically identical to the corresponding bond length found in **5** [2.134(5) Å]. The W(VI)≡C distance in **6** is 1.759(4) Å, which is statistically identical to the bond length of 1.755(2) Å found in $(ArO)_2(CH_3)_3CCH_2W{\equiv}CC(CH_3)_3$ but 0.011(4) Å longer than that in **5**, perhaps due to a small contribution from the trans influence of THF.

Broad signals in the ^1H NMR spectrum of **6** (C_6D_6) at 4.07, 3.40, 1.45, and 1.16 ppm, each integrating to four protons, indicate that two symmetrically unique THF molecules coordinate to the W(VI) ion. Distinct resonances for the ^{t}Bu and alkylidyne protons appear at 1.65 and 0.61 ppm, respectively, indicating that **6** is also C_s-symmetric. A downfield resonance at 320.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum is attributable to the W≡C carbon, and a resonance at 193.5 ppm corresponds to the $W{-}C_{pincer}$.

Table 1. Results of PA Polymerization by 6[a]



R	yield (%)	activity[b]	TON	M_w (Da)	M_w/M_n
H	66	6.70×10^5	3280	35 188	4.28
F	87	1.05×10^6	4371	20 480	3.65
MeO	47	6.20×10^5	2346	20 637	3.33

[a] Substrate (1000 μmol) was added to **6** (0.20 μmol) in toluene (0.5 mL) for 30 min at 25 °C, after which the reaction was quenched and polymer washed with methanol. [b] Units: $g_{PPA}\ mol_{cat}^{-1}\ h^{-1}$.

Complex **6** catalyzes PPA synthesis (Table 1). Polymer characterization includes FTIR and ^1H NMR spectroscopy as well as gel-permeation chromatography (GPC) to determine M_w and M_w/M_n. Complex **6** polymerizes PA, 1-ethynyl-4-fluorobenzene (*p*-F-PA), and 1-ethynyl-4-methoxybenzene (*p*-MeO-PA). The monomers all absorb IR radiation near 3300 and 2100 cm^{-1}, corresponding to the ≡C−H and C≡C stretching vibrations, respectively (see the SI). Both bands disappear in the IR spectra of the PPAs and are replaced with a new band near 1595 cm^{-1}. The ^1H NMR spectra of the polymers in $CDCl_3$ reveal broad resonances at 6.7 and 5.8 ppm, confirming the presence of $(-CH{=}CPh-)_n$ units. Integrating the *cis*-vinyl proton relative to the *trans*-vinyl proton and the aromatic protons provides an approximate value for the cis/trans content of the double bond within the polymers.[21] The R-PPA polymers are orange and contain a high ratio of cis double bonds (PPA, 90%; *p*-F-PPA and *p*-MeO-PPA, 70−80%). For comparison, Rh catalysts typically provide high-cis-content PPA with a head-to-tail microstructure.[3b] To evaluate the microstructure of the polymer, the PPA sample was heated at 215 °C and then examined for the presence of cyclized products according to known methods.[22] The ^1H NMR spectrum of the heated PPA reveals signals attributable to 1,3,5- and 1,2,4-triphenylbenzene in a 94:6 ratio, indicative of a microstructure containing predominately head-to-tail units. It is plausible that if the ring expansion mechanism operates, the polymers may be cyclic; however, we were unable to elucidate their macrostructure. All three polymers have high M_w (PPA, 35 188 Da; *p*-F-PPA, 20 480 Da; *p*-MeO-PPA, 20 637 Da), and the polydispersities (M_w/M_n) are modest (PPA, 4.28; *p*-F-PPA, 3.65; *p*-MeO-PPA, 3.33).[3b] More striking is the activity of **6** and its high turnover number (TON), exemplified in the polymerization of *p*-F-PA (activity = 1.05×10^6 $g_{PPA}\ mol_{cat}^{-1}\ h^{-1}$, TON = 4371). It is plausible that metathesis products may form during the time scale of the reaction, but periodic GC analysis of the polymerization solution did not indicate the presence of diphenylacetylene or ethyne.

In conclusion, trianionic pincer W−alkylidyne complexes are now synthetically accessible. The critical synthetic strategy is first to attach the ligand onto the W ion as a diphenolate to form **3**. Prior attempts with the peralkyl $Np_3W{\equiv}CC(CH_3)_3$ (Np = neopentyl) resulted in $C_{ipso}{-}H$ bond activation of the pincer across the W≡C bond to form an alkylidene.[13e] Once the ligand is attached as a diphenolate, simple addition of the mild base $Ph_3P{=}CH_2$ deprotonates the $C_{ipso}{-}H$ proton to generate the anionic-pincer-supported alkylidyne $\{[^tBuOCO]W{\equiv}CC(CH_3)_3(O^tBu)\}\{PPh_3CH_3\}$ (**4**). Addition of methyl triflate to **4** in Et_2O provides the corresponding neutral complex $[^tBuOCO]W{\equiv}CC(CH_3)_3(Et_2O)$ (**5**) as a mixture containing phosphonium triflate. However, addition of THF displaces the Et_2O ligand in **5**, thus subtly changing the solubility and allowing the isolation of $[^tBuOCO]W{\equiv}CC(CH_3)_3(THF)_2$ (**6**) in high yield and purity.

Complex **6** is a highly active catalyst for the polymerization of phenylacetylenes. Relative to other metal−alkylidyne catalysts for the polymerization of PAs, **6** is the most active.[7a−c] The high activity is attributable to the inherent ligand geometry, which creates a coordinatively unsaturated catalyst. Constraining the three anionic donor ligands to the meridional plane, thereby providing easy access to an open coordination site, promotes the coordination and insertion of PA units. Furthermore, the tridentate trianionic pincer ligand renders the precatalyst sufficiently stable to be isolable and long-lived (TON >4000), a quality we are currently exploiting to elucidate the polymerization mechanism.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and 2D NMR spectra, IR spectra, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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