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Synthesis and Characterization of a Molybdenum Alkylidyne Supported by a Trianionic OCO^{3-} Pincer Ligand

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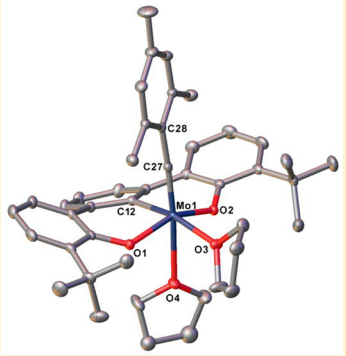
Supporting Information

ABSTRACT: This report details the preparation of the trianionic pincer ligand supported Mo−alkylidyne complex [^{t}BuOCO]Mo≡CMes(THF)$_2$ (**5**). The catalytic activity of [^{t}BuOCO]Mo≡CMes(THF)$_2$ (**5**) for alkyne polymerization is limited in contrast to its W-congener. Solution and crystallographic evidence for the conversion of the trianionic pincer complex [^{t}BuOCO]Mo≡CMes(THF)$_2$ (**5**) to a tetraanionic pincer complex [O_2C-(MesC═)Mo(η^2-CH≡C^{t}Bu)(THF)] (**6**) upon exposure to *tert*-butylacetylene is provided.



INTRODUCTION

Trianionic pincer and pincer-type ligands[1] confine three anionic donors to a meridional coordination sphere thereby creating metal complexes with both electronic and coordination unsaturation. When ligated to group 6 high oxidation state W-alkylidynes,[2−6] trianionic pincer and pincer-type ligands engender unique reactivity not seen among similar group 6 alkylidynes bearing monodentate ligands. For example, the W-alkylidyne complex[7] [^{t}BuOCO]W≡C^{t}Bu(THF)$_2$ reacts with phenylacetylene to afford the tetraanionic pincer W-alkylidene, [O_2C(^{t}BuC═)W(η^2-CH≡CPh)(THF)],[8] which catalyzes the polymerization of alkynes into high molecular weight cyclic polyalkynes.[9] The complex [^{t}BuOCO]W≡C^{t}Bu(THF)$_2$ initiates the polymerization of norbornene (NBE) to generate >95% *cis*, *syndiotactic* cyclic polyNBE.[10] The alkylidyne [^{t}BuOCO]W≡C^{t}Bu(THF)$_2$ also cleaves CO_2 in a stoichiometric reaction to produce the tetraanionic pincer W-oxo alkylidene complex, [O_2C((CO)^{t}BuC═)W≡O(THF)], which can also initiate the polymerization of norbornene to give >98% *cis*, *syndiotactic* cyclic polyNBE.[11] An analogous ONO^{3-} trianionic W-alkylidyne complex, [CF_3−ONO]W≡C^{t}Bu(THF)$_2$ deoxygenates carbonyl containing substrates in a Wittig-like manner[12−14] with rates up to 4 orders of magnitude faster than (DIPP)$_3$W≡C^{t}Bu.[12,15,16] The complex [CF_3−ONO]W≡C^{t}Bu(THF)$_2$ is one of the only reported high oxidation state W-alkylidynes to react with ethylene and norbornene in a "Ynene" reaction to produce cyclic polyNBE.[10]

Conspicuously absent from the diverse profile of reactions described above are trianionic pincer ligand supported *molybdenum* alkylidynes.[17] This is due in part to the difficulty with accessing molybdenum alkylidynes in general, with only a handful of synthetic protocols affording them reliably and in good yields. Access to molybdenum alkylidynes utilizes one of four routes:[18] (a) the high oxidation state scheme discovered by Schrock, involving the synthesis of Mo≡C^{t}Bu-(CH_2^{t}Bu)$_3$;[19−21] (b) the more commonly employed low oxidation state route starting from Mo(CO)$_6$, pioneered by Mayr;[22−24] (c) the addition of $RCHCl_2$ to Cummins' Mo(NAr^{t}Bu)$_3$[25−28] to generate Mo≡CR(NAr^{t}Bu)$_3$, developed by Fürstner and Moore;[29−32] and (d) the recent nitride alkyne cross metathesis (NACM) of Mo≡N(OCMe(CF_3)$_2$)$_3$ with 3-hexyne, exploited by Johnson.[33−35] While the Schrock synthesis provides exclusive access to alkylidynes containing the neopentylidyne fragment, Mo≡C^{t}Bu, the reaction is not reliably scalable.[36] The low oxidation state protocol is scalable and generates Mo-alkylidynes containing *aryl* substituents on the alkylidyne. The NACM route is tedious in that copious polymer is generated during cross-metathesis; however, the resulting molybdenum propylidyne (Mo≡CEt) affords great flexibility as subsequent metatheses can yield many different alkylidynes.[37,38] Tungsten alkylidynes, on the other hand, are reliably accessed employing methods ranging from the metathesis of alkynes across W≡W triple bonds,[39,40] to the low-oxidation state route employing W(CO)$_6$.[22−24]

With numerous recent reports from the groups of Tamm,[41−45] Fürstner,[46,47] and Fischer[48−50] focusing on the synthesis of Mo-alkylidynes generated through the low

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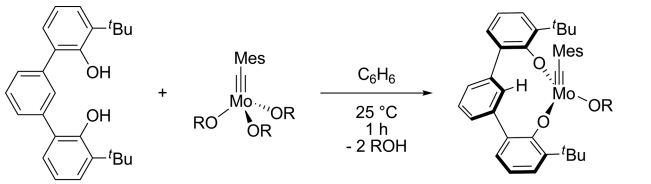
oxidation state scheme, it seemed reasonable to explore a Mo-based catalyst for cyclic polymer synthesis. Some of the advantages over tungsten include potentially higher rates of activity, functional group tolerance, ease of Mo-alkylidyne synthesis via the low oxidation state route, and access to alkylidynes bearing various aryl substituents. Specifically, we targeted metalating Mo≡CMes(OCMe(CF_3)$_2$)$_3$,[43] known for its superior ability to tolerate **t**erminal **a**lkynes in **m**etathesis (TAM)[43,51] reactions.

This report communicates the synthesis of the first trianionic pincer ligand supported Mo-alkylidyne complex, [^{t}BuOCO]-Mo≡CMes(THF)$_2$. Preliminary reactivity studies suggest [^{t}BuOCO]Mo≡CMes(THF)$_2$ undergoes reductive migratory insertion when exposed to terminal alkynes, analogous to [^{t}BuOCO]W≡C^{t}Bu(THF)$_2$,[7] but polymerization activity is low and the topology of the polymers formed could not be determined.

RESULTS AND DISCUSSION

Addition of either KO^{t}Bu or KO(CMe(CF_3)$_2$) to Mo≡CMesBr$_3$(DME) in THF readily generates the alkylidynes Mo≡CMes(OR)$_3$ [where R = O^{t}Bu (**1**) or O(CMe(CF_3)$_2$) (**2**)].[52] Combining proligand [^{t}BuOCO]H$_3$ with either **1** or **2** in benzene at ambient temperature results in metalation. The reaction generates the dianionic pincer ligand containing product, [^{t}BuOC*H*O]Mo≡CMes(OR) [where R = O^{t}Bu (**3a**) or OCMe(CF_3)$_2$ (**3b**)], with extrusion of two equiv of the corresponding alcohol (Scheme 1). Removal of the liberated

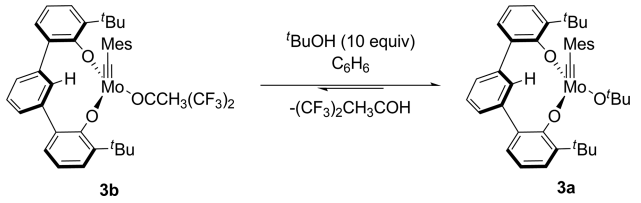
Scheme 1. Metalation of the [^{t}BuOCO]H$_3$ Proligand with Mo≡CMes(OR)$_3$ where R = O^{t}Bu or OCMe(CF_3)$_2$



alcohol *in vacuo* followed by triturating with pentane affords **3a** and **3b** in 87% and 93% isolated yields, respectively, as bright yellow powders of sufficiently high purity for further use. The presence of a single resonance in the ^{1}H NMR spectrum (C_6D_6) for the *ortho*-^{t}Bu protons indicates both **3a** and **3b** are C_s symmetric in solution. Consistent with the presence of mirror symmetry, only one set of aromatic resonances appear for the [^{t}BuOCO]$^{3-}$ pincer ligand backbone, and the *ipso* C−H proton on the central ring of the pincer ligand resonates at 8.19 and 7.43 ppm for **3a** and **3b**, respectively. Typical downfield resonances for the alkylidyne C_α-atom appear at 303.3 and 313.3 ppm for **3a** and **3b**, respectively. The chemical shifts measured in C_6D_6 for the parent complexes appear at 297.4 ppm for Mo≡CMes(O^{t}Bu)$_3$ and 317.6 ppm for Mo≡CMes(OCMe(CF_3)$_2$)$_3$.[43,52]

The nature of the alkoxide within **3** is crucial as its eventual loss affords the neutral trianionic pincer complex (*vide infra*). It is preferable for the alkoxide to be -O^{t}Bu considering the chemistry already established for the W-analog.[7] Though **3a** is accessible directly through metalation, treating complex **3b** with ten equiv of ^{t}BuOH converts it to **3a** (Scheme 2). The use

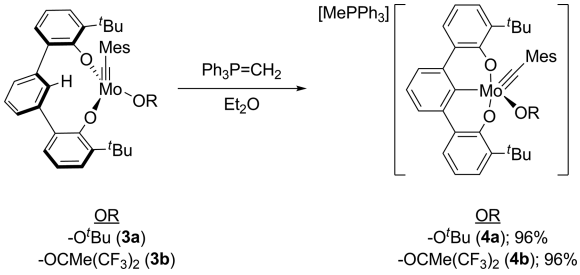
Scheme 2. *tert*-Butanol Mediated Alcoholysis of 3b To Generate 3a



of excess ^{t}BuOH facilitates the displacement of the weakly basic -OCCH$_3$(CF_3)$_2$ by shifting the equilibrium in favor of **3a**. There is precedent for similar alkoxide substitution reactions within W≡CR,[53] Mo≡N,[54] and Mo≡Mo systems.[55]

The next step in the protocol leading to the neutral trianionic pincer complex involves deprotonating **3a** with the phosphorus ylide, $Ph_3P{=}CH_2$ (Scheme 3).[56,57] Combining

Scheme 3. Synthesis of the Anionic Mo-Alkylidynes 4a and 4b



ethereal solutions of $Ph_3P{=}CH_2$ and **3a** results in the successful removal of the *ipso* C−H proton within **3a** by the mild base. Initially, a tacky red solid forms, and then multiple pentane triturations produce **4a** as a red microcrystalline material. Despite its poor solubility in most solvents, the identity of **4a** is unambiguously ascertained through the lack of the *ipso* C−H proton resonance in its ^{1}H NMR spectrum. Furthermore, within the ^{13}C{^{1}H} NMR spectrum of **4a** in C_6D_6, the C_{ipso} resonates at 194.4 ppm, which is downfield of the resonance in **3a** found at 114.9 ppm and is diagnostic for successful attachment of the pincer backbone to the metal center. Previously reported trianionic pincer ligand supported W-anionic alkylidynes[7,8,53] exhibit similar downfield C_{ipso} resonances. Analogously, deprotonating **3b** yields **4b** as a yellow solid (96% isolated yield) with a characteristic ^{1}H NMR spectrum (see ESI).

The final step in the synthesis of the neutral trianionic pincer Mo-alkylidyne complex relies on the MeOTf-induced displacement of -O^{t}Bu within **4a** as MeO^{t}Bu and concomitant loss of the phosphonium cation as its triflate salt (Scheme 4). This protocol works successfully for W-alkylidynes supported by both the [CF_3−ONO]$^{3-}$ and the [^{t}BuOCO]$^{3-}$ ligands.[3,7] The same reaction, however, fails with **4b** presumably due to the presence of the weakly nucleophilic -OCMe(CF_3)$_2$ ligand. Following the synthetic scheme established for similar W-alkylidynes,[3,7] addition of cold methyl triflate (neat) to the prechilled (−35 °C) Mo-alkylidyne **4a** dissolved in an 80:20 (v/v) mixture of Et_2O and THF produces an immediate color change from red to dark brown/black. After workup [^{t}BuOCO]Mo≡CMes(THF)$_2$ (**5**) is isolated as an orange colored analytically pure solid.

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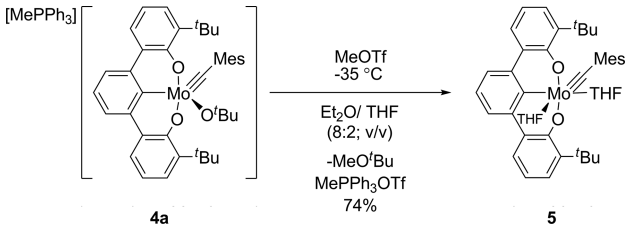
Scheme 4. Synthesis of the Neutral Mo−Alkylidyne Complex 5 through MeOTf-Induced Displacement of the -O^{t}Bu Ligand in 4a



The ^{1}H NMR spectrum of **5** in C_6D_6 exhibits resonances consistent with the assigned C_s symmetric complex; a single resonance appears for both the *ortho*-^{t}Bu protons at 1.63 ppm. The lack of a resonance for -O^{t}Bu protons confirms its displacement. Most noticeable within the ^{1}H NMR spectrum of **5** is the presence of two broad resonances at 1.39 and 3.71 ppm, each integrating to 8H, for the two bound THF molecules. This spectroscopic feature is reminiscent of the W-analog, [^{t}BuOCO]W≡C^{t}Bu(THF)$_2$, which also binds to two molecules of THF.[7] The C_{ipso} of the central pincer aryl ring resonates at 187.0 ppm within the ^{13}C{^{1}H} NMR spectrum of **5** (C_6D_6). This downfield value offers support for its assignment as an anionic (X-type) ligand.[58,59]

Unequivocal evidence for the structure of **5** comes from a single crystal X-ray diffraction experiment performed on crystals that deposit from a cold ethereal solution of **5** (Figure 1). The asymmetric unit of **5** consists of the Mo complex and one diethyl ether solvent molecule. One THF ligand exhibits disorder and is modeled and refined in two parts. The complex

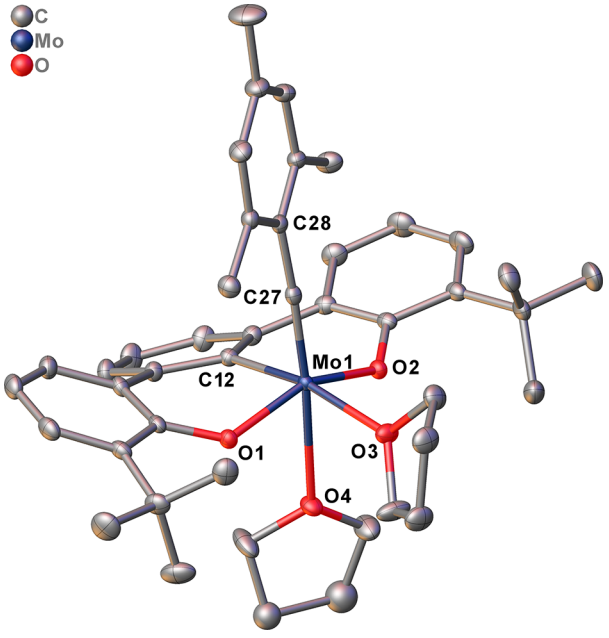


Figure 1. Molecular structure of [^{t}BuOCO]Mo≡CMes(THF)$_2$ (**5**) with ellipsoids drawn at the 50% probability level. Hydrogen atoms, disordered THF molecules, and lattice solvent molecule (diethyl ether) are removed for clarity. Selected bond distances [Å]: Mo1−C12 2.1479(13), Mo1−C27 1.7676(13), Mo1−O1 1.9498(9), Mo1−O2 1.9256(9), Mo1−O3 2.2381(10), Mo1−O4 2.5281(10). Selected bond angles [deg]: ∠Mo1−C27−C28 177.28(10), ∠C12−Mo1−O3 166.69(4), ∠C27−Mo1−O4 174.33(4), ∠O1−Mo1−O2 151.07(4).

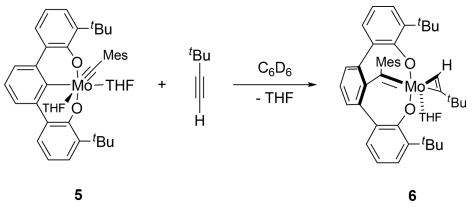
adopts a distorted octahedral coordination geometry with the [^{t}BuOCO]$^{3-}$ ligand and a THF molecule occupying one plane. The mesityl alkylidyne and the second THF molecule are *trans* to each other.

An approximate plane bisecting the molecule in equal halves in the solid-state structure mirrors the solution state C_s symmetry. The Mo1−C12 bond distance of 2.1479(13) Å is similar to that observed for [^{t}BuOCO]W≡C^{t}Bu(THF)$_2$, measured at 2.132(3) Å.[7] A short Mo1≡C27 distance of 1.7676(13) Å is strong evidence for a Mo≡C triple bond. For comparison, the same distance within Mo≡CMes(O^{t}Bu)$_3$ is 1.747(3) Å,[52] 1.747(2) Å in Mo≡CMes(OCMe$_2$(CF$_3$))$_3$,[52] 1.7438(16) Å in Mo≡CMes(OCMe(CF$_3$)$_2$)$_3$,[43] 1.7429(16) Å in Mo≡CMes(OC(CF$_3$)$_3$),[44] and 1.759(4) Å in [^{t}BuOCO]-W≡C^{t}Bu(THF)$_2$.[7] The ∠Mo≡C—C angle lends further evidence for the presence of the Mo≡C triple bond. Within **5**, this angle measures 177.28(10)°. The same angles for Mo≡CMes(O^{t}Bu)$_3$[52] and Mo≡CMes(OC(CF$_3$)$_3$)[44] measure 176.3(2)° and 173.86(13)°, respectively. The THF molecules expectedly display variable bond lengths. The THF molecule bound *cis* to the alkylidyne ligand displays a short 2.2381(10) Å Mo−O bond distance, whereas the THF *trans* to the alkylidyne ligand exhibits a longer Mo−O bond length of 2.5281(10) Å. Presumably, the alkylidyne ligand exerts a stronger *trans* influence relative to the Mo−C$_{pincer}$ bond.

Exposing [^{t}BuOCO]Mo≡CMes(THF)$_2$ (**5**) to excess phenylacetylene results in low molecular weight (10,000−15000 g/mol) polymer formation, and the activity (76,500 g$_{pol}$/mol$_{cat}$/h) pales in comparison to the tungsten initiator [^{t}BuOCO]W≡C^{t}Bu(THF)$_2$ (1,050,000 g$_{pol}$/mol$_{cat}$/h).[7−9] Variations in the catalyst to monomer ratio, solvent, and temperature did not influence polymerization activity or yield. Broad dispersities (>2.0) and low molecular weights hamper the light scattering data, and as a consequence meaningful conclusions regarding the topology of the polymers could not be obtained. (Refer to the Supporting Information for details on the polymerization trials).

The complex Mo≡CMes(OCMe(CF$_3$)$_2$)$_3$ was chosen for metalation with the ^{t}BuOCO^{3-} ligand owing to its superior ability to tolerate terminal alkynes during metathesis trials.[43] Though complex **5** is not an active alkyne polymerization catalyst, it was important to assess *in situ* whether the trianionic pincer converts to a tetraanionic pincer akin to the W-analog.[8,9] In an NMR tube (C_6D_6), treating complex **5** with *tert*-butylacetylene results in the formation of the tetraanionic pincer complex [O$_2$C(MesC═)Mo(η^2-CH≡C^{t}Bu)(THF)] (**6**) (Scheme 5). *In situ* characterization via NMR spectroscopy confirms the identity of **6**. Most compelling in the ^{1}H NMR spectrum of **6** is a characteristic downfield alkyne C−*H* resonance at 10.41 ppm for the η^2-bound ^{t}BuCC*H*. Further evidence for the formation of the Mo-complex **6** comes from the ^{13}C chemical shift for the C_{ipso} of the central pincer aryl

Scheme 5. *In Situ* Formation of Complex 6 Featuring a Tetraanionic Pincer Ligand and Bound η^2-Alkyne



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ring. The C_{ipso} within **6** resonates at 125.7 ppm, which is 61.4 ppm upfield of the value found in **5** (187.0 ppm). The C_{ipso} for an analogous W-complex also shifts 61 ppm upfield for the equivalent trianionic (193.5 ppm) to tetranionic (132.5 ppm) ligand conversion.[9] A minor impurity (~6%) is also present in solution, but its identity could not be determined. (See the accompanying Supporting Information for a detailed solution-phase assignment for the structure of **6** via 2D NMR and NOE analyses).

The molecular structure of **6** (Figure 2) determined by a single crystal X-ray diffraction experiment corroborates the

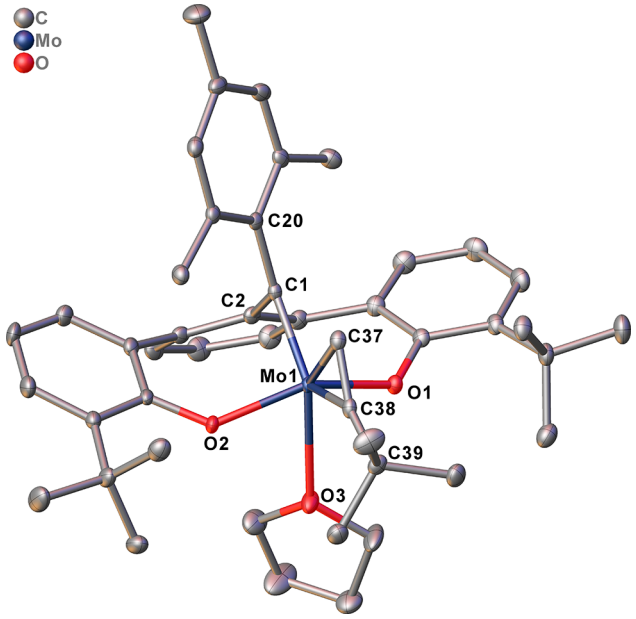

Figure 2. Molecular structure of [O_2C(MesC═)Mo(η^2-CH≡C^{t}Bu)(THF)] (**6**) with ellipsoids drawn at the 50% probability level. Hydrogen atoms, disordered THF molecule, and lattice solvent molecule (benzene) are removed for clarity. Selected bond distances [Å]: Mo1 = C1 1.9072(11), C1−C2 1.5318(15), Mo1−O1 1.9605(8), Mo1−O2 1.9839(8), Mo1−O3 2.4303(9), Mo1−C37 2.0105(11), Mo1−C38 2.0444(12), C37−C38 1.3020(16). Selected bond angles [deg]: ∠O1−Mo1−O2 146.71(3), ∠C2−C1−Mo1 90.80(7), ∠Mo1−C37−C38 72.69(7), ∠Mo1−C38−C37 69.86(7), ∠C37−Mo1−C38 37.45(5).

solution phase *tetraanionic* assignment (*vide supra*). The C_{ipso} of the central pincer aryl ring inserts into the mesityl alkylidyne ligand (in **5**), transforming it into a disubstituted alkylidene. The alkylidene ligand and the phenoxides form the tetraanionic core in **6**, occupying three of the six vertices constituting a *distorted* octahedral geometry. The η^2-bound *tert*-butylacetylene and THF ligands occupy the remaining vertices. The Mo═C1 bond length of 1.9072(11) Å within **6** is significantly longer than the Mo≡C bond length of 1.7676(13) Å observed in **5** and is comparable to other similar structurally characterized *neutral* Mo(VI)-disubstituted alkylidenes, whose Mo═C bond lengths typically range from 1.87 to 1.96 Å.[17,60−62] Best described as a metallacyclopropene the η^2-bound *tert*-butylacetylene has an elongated C37−C38 bond length of 1.3020(16) Å (*cf.* 1.2 Å for a typical C≡C)[63,64] and a ∠C37−C38−C39 angle of 143.65(11)°.

CONCLUSION

In summary, this work describes the synthesis of the first trianionic pincer ligand supported Mo-alkylidyne, [^{t}BuOCO]-Mo≡CMes(THF)$_2$ (**5**). Exposure of complex **5** to alkynes, in the case of *tert*-butylacetylene converts it from a trianionic pincer Mo-alkylidyne to the tetraanionic pincer complex **6** in an identical fashion to the highly active tungsten catalyst previously reported.[8] The tetraanionic form is the proposed active catalyst for alkyne polymerization leading to cyclic polyalkynes.[9] Despite its propensity to achieve the tetraanionic form, complex **5** exhibits low activity for polymerization of phenylacetylene that may be due in part to the large mesityl group on the alkylidyne.[65] The important feature of this work though pertains to the synthesis of **5**. Trianionic pincer molybdenum alkylidynes should now be accessible via the low oxidation state synthesis method of Mo-alkylidynes. As more multianionic pincer ligands become available, this work will be useful for providing guidance in generating new trianionic pincer Mo-alkylidynes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00677.

Full experimental details, including NMR data and spectra for new compounds, and X-ray crystal structure data (PDF)

Accession Codes

CCDC 1862886 and 1870872 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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