

Syntheses of Molybdenum Oxo Alkylidene Complexes through Addition of Water to an Alkylidyne Complex

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Supporting Information

ABSTRACT: Addition of one equiv of water to Mo-(CAr)[OCMe(CF₃)₂]₃(1,2-dimethoxyethane) (**2**, Ar = *o*-(OMe)C₆H₄) in the presence of PPhMe₂ leads to formation of Mo(O)(CHAr)[OCMe(CF₃)₂]₂(PPhMe₂) (**3**(PPhMe₂)) in 34% yield. Addition of one equiv of water alone to **2** produces the dimeric alkylidyne hydroxide complex, {Mo(CAr)[OCMe(CF₃)₂]₂(μ-OH)}₂(dme) (**4**(dme)) in which each bridging hydroxide proton points toward an oxygen atom in an arylmethoxy group. Addition of PMe₃ to **4**(dme) gives the alkylidene oxo complex, **3**(PMe₃), an analogue of **3**(PPhMe₂) (95% conversion, 66% isolated). Treatment of **3**(PMe₃) with two equiv of HCl gave Mo(O)(CHAr)Cl₂(PMe₃) (**5**), which upon addition of LiO-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃ (LiOHIPT) gave Mo(O)(CHAr)-(OHIPT)Cl(PMe₃) (**6**). Compound **6** in the presence of B(C₆F₅)₃ will initiate the ring-opening metathesis polymerization of cyclooctene, 5,6-dicarbomethoxynorbornadiene (DCMNBD), and *rac*-5,6-dicarbomethoxynorbornene (DCMNBE), and the homocoupling of 1-decene to 9-octadecene. The poly(DCMNBD) has a *cis,syndiotactic* structure, whereas poly(DCMNBE) has a *cis,syndiotactic,alt* structure. X-ray structures were obtained for **3**(PPhMe₂), **4**(dme), and **6**.

A tungsten oxo alkylidene complex was the first high oxidation state complex to be prepared that would react with an olefin to give the new alkylidene expected from olefin metathesis.^{1,2} Oxo alkylidene complexes of Mo and W, M(O)(CHR)(OSi_{surf})₂, are also thought to be the active sites in classical catalysts prepared from metal oxides on silica.³ However, imido alkylidene complexes were chosen for development of olefin metathesis chemistry⁴ because an imido ligand is less likely than an oxo ligand to bridge between metals⁵ or to be attacked by an electrophile and removed from the metal.^{6,7} A new approach to tungsten oxo alkylidenes⁸ allowed several examples that contain sterically demanding ligands to be prepared and their reactions explored,⁹ but isolable molybdenum oxo alkylidene complexes that are active for metathesis of olefins have remained elusive.

Two crystallographically characterized molybdenum oxo alkylidene thiolate complexes were prepared serendipitously from Mo(IV) thiolate hydride complexes, phenylacetylene, and water,¹⁰ but no olefin metathesis activities were reported. In

2015, the Mo oxo alkylidene complex, Mo(O)(CHSiMe₃)[NP(*t*-Bu)₃]₂, was prepared relatively straightforwardly and in high yield via α abstraction in a five-coordinate bistrimethylsilylmethyl intermediate.¹¹ Unfortunately, the steric and electronic properties of the [NP(*t*-Bu)₃]₂⁻ ligand prevent facile initiation of olefin metathesis reactions, even upon “activating” Mo(O)-(CHSiMe₃)[NP(*t*-Bu)₃]₂ through addition of B(C₆F₅)₃ to the oxo ligand.^{9b,11} (Addition of B(C₆F₅)₃ to an oxo ligand has been shown to accelerate ROMP reactions with tungsten-based oxo alkylidene initiators by at least two orders of magnitude.^{9c})

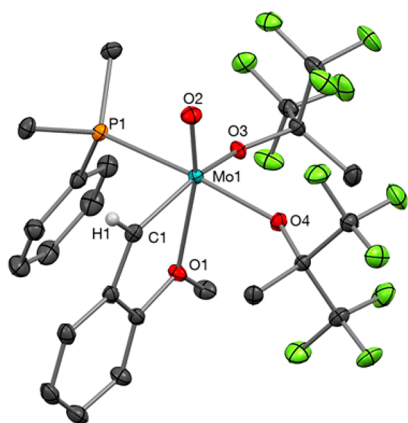
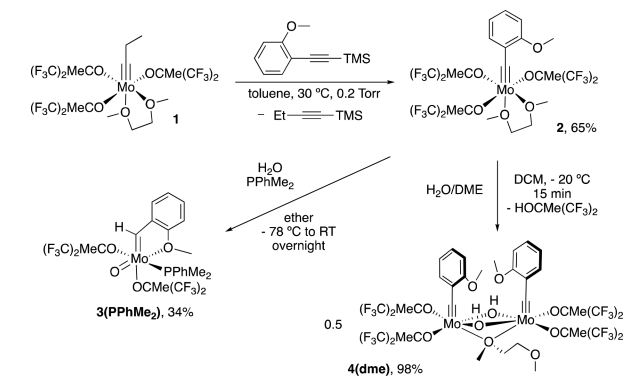
In 1981, Wengrovius¹² noted in his Ph.D. thesis that W(*C-t*-Bu)(PMe₃)₃Cl₃ reacts with one equivalent of water in CH₂Cl₂ to give W(O)(CH-*t*-Bu)(PMe₃)₂Cl₂ and Me₃PHCl in essentially 100% yield. Wengrovius’ result provided inspiration for the synthesis of the first imido alkylidene of tungsten by moving a proton from an amido ligand to an alkylidyne carbon atom.¹³ More recently, Veige has reported conversion of a tungsten alkylidyne into a tungsten oxo alkylidene,¹⁴ and theoretical studies have addressed movement of protons in the primary coordination sphere of high oxidation state complexes.¹⁵ Because molybdenum(VI) alkylidyne complexes can now be prepared from Fisher-type alkylidenes,¹⁶ reactions between a Mo alkylidyne complex and water would seem to be a plausible approach to the synthesis of Mo oxo alkylidene complexes. We have now prepared Mo oxo alkylidene complexes in this manner that are reactive in olefin metathesis reactions. To our knowledge, these are the first examples of well-characterized and metathetically active molybdenum oxo alkylidene complexes.

The reaction between **1**^{16a} and C₆H₄(*o*-OMe)C≡CTMS gave **2** in moderate yield (Scheme 1). Addition of one equiv of water to **2** in the presence of one equiv of PPhMe₂ led to **3**(PPhMe₂) in 34% yield. An X-ray study of **3**(PPhMe₂) (Figure 1) confirmed that the alkylidene is orientated in the *anti* manner ($J_{\text{CH}\alpha} = 140$ Hz), i.e., with the methoxide oxygen in the *o*-methoxybenzylidene ligand coordinated *trans* to the oxo ligand (Mo1–O1 = 2.4740(8) Å). An exploration of PMe₃, PEt₃, P(*i*-Pr)₃, and PPh₂Me in the reaction between **2** and water revealed that a product analogous to **3**(PPhMe₂) is formed only in the case of PMe₃ (**3**(PMe₃), 25% yield). Curiously, a different product was obtained in *high* yield in the presence of P(*i*-Pr)₃, but it does not contain P(*i*-Pr)₃. In fact, **2** reacts with one equivalent of water (in

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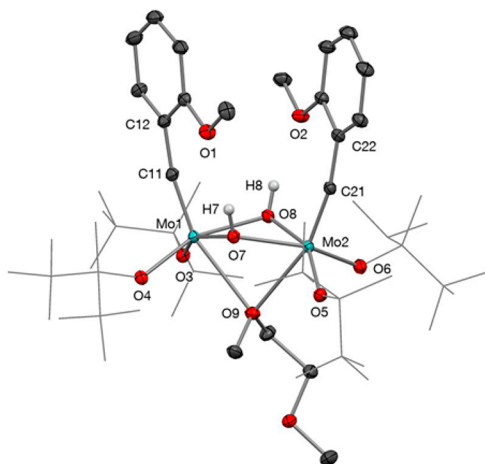
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Scheme 1

Figure 1. Drawing of the X-ray structure of 3(PPhMe₂).

dme) in the absence of any phosphine at $-20\text{ }^{\circ}\text{C}$ to give one equiv of hexafluoro-*t*-butanol per Mo and a product (**4(dme)**, Scheme 1) that exhibits a sharp resonance for a single proton (per Mo) at 9.38 ppm in its proton NMR spectrum. One equivalent of water (in dme) reacts with **4(dme)** relatively slowly (13% decomposition in 20 min, 54% in 19 h, at $22\text{ }^{\circ}\text{C}$; see SI) to give unidentified products and a black precipitate, a result that accounts for the high yield of **4(dme)** under the reaction conditions.

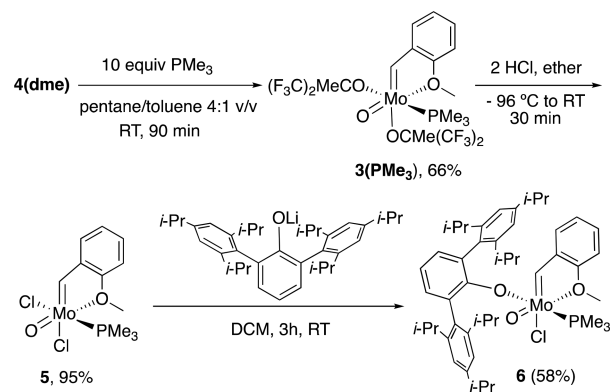
An X-ray structural study showed that **4(dme)** is a dimeric hydroxy alkylidene complex (Figure 2; Mo1–Mo2 = 3.2164(2)

Figure 2. Drawing of the X-ray structure of **4(dme)**.

Å). The benzylidene ligands are tipped slightly toward the bridging hydroxides (Mo2–C21–C22 = $167.33(7)^{\circ}$; Mo1–C11–C12 = $168.57(7)^{\circ}$) and turned so that the methoxy oxygen in each benzylidene ligand is situated over the hydroxy protons (H7 and H8), which were located. The O(methoxy)⋯O(hydroxy) distances are 2.904 and 2.814 Å, the OH⋯O distances are 2.134 and 2.026 Å, and the O–H⋯O angles are 163.75° and 158.82° . IR data ($\nu_{\text{OH}} = 3482\text{ cm}^{-1}$ in the solid; see SI), O⋯O distances, and the fact that phenyl ethers are poor H-bond acceptors, all suggest that these O⋯H–O arrangements are essentially purely electrostatic,¹⁷ i.e., the hydroxyl hydrogen is positioned to minimize repulsions between electron pairs on O1 vs O7 and O2 vs O8. (A more significant interaction between a hydroxide hydrogen and a methoxyphenyl oxygen was invoked in *trans*-Pt(PET₃)₂(*o*-MeOC₆H₄)(Br)(OH)(CN) on the basis of X-ray studies (O⋯O = 2.722 Å) and chemistry ascribable to a hydroxy radical generated under photochemical conditions.¹⁸) A six-coordinate geometry around each Mo is reached when *one* oxygen in a dimethoxyethane (O9) bridges between the two Mo atoms (Mo–O = 2.4743(7) and 2.5487(7) (7) Å). A proton NMR spectrum of **4(dme)** in CD₂Cl₂ in the presence of 13 equiv of diethyl ether shows it to consist of a mixture of **4(dme)** ($\delta_{\text{OH}} = 9.30\text{ ppm}$) and **4(ether)** ($\delta_{\text{OH}} = 9.24\text{ ppm}$) in a ratio of 37:63 (see SI). This evidence suggests that the weakly bound dme has little to do in terms of maintaining the dimeric integrity of **4(dme)**.

The reaction between **4(dme)** and PPhMe₂ in pentane gave **3(PPhMe₂)** in ~30% yield, approximately the same as in the reaction between **2** and water in the presence of PPhMe₂ (34% yield). However, a reaction between **4(dme)** and ten equivalents of PMe₃ (five equivalents of PMe₃ per Mo; Scheme 2) gave

Scheme 2



3(PMe₃) isolated in 66% yield. The key mechanistic question is exactly how does a given hydroxy proton find its way to one or the other alkylidene carbon atom? Displacement of the weakly bridging dme by an incoming phosphine would seem to be a good starting point toward ultimately cleaving dimeric **4(dme)** and promoting or assisting movement of a proton from OH to the benzylidene carbon atom. Although we cannot exclude the possibility that Me₃PH⁺ is formed as part of the process of moving the proton from O to C to form the alkylidene, it also seems plausible that the proton transfers directly from O to C in the more crowded environment created when PMe₃ binds to Mo and begins to cleave the dimer. Proton transfer from C_α in an alkyl ligand to C_α in another alkyl ligand to give an alkylidene and alkane (“ α hydrogen abstraction”) is also accelerated through

coordination of PMe_3 and other donor ligands in a variety of circumstances.⁴

We were somewhat surprised to find that addition of two equiv of HCl to $3(\text{PMe}_3)$ produced **5** (Scheme 2) in 95% yield. Compound **6** could then be prepared in 58% yield on a gram scale through addition of LiOHIPT to **5** (OHIPT = O-2,6-(2,4,6-*i*-PrC₆H₂)₂C₆H₃). An X-ray study revealed **6** to have the structure shown in Figure 3. The bond distances are in the range

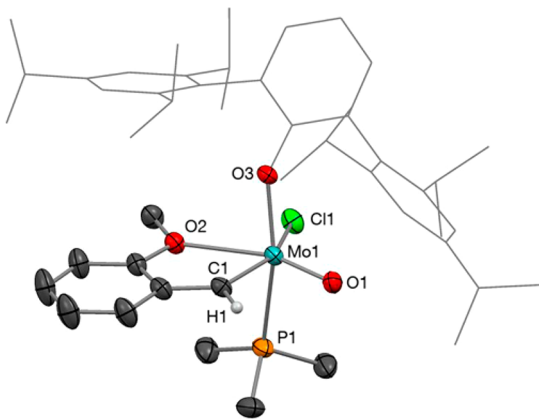


Figure 3. Drawing of the X-ray structure of **6**.

found in related monoaryloxide monochloride phosphine adducts reported recently,¹⁹ and the Mo1–O2 distance in the *anti* alkylidene (2.514(2) Å) is close to the analogous Mo1–O1 distance in $3(\text{PPhMe}_2)$ (2.4740(8) Å; Figure 1). Compound **5** would be an attractive starting point for the synthesis of other oxo alkylidene derivatives, especially if it, or some analogue, could be prepared in fewer steps.

We have explored the metathesis activity of **6** in a preliminary fashion (Table 1). Although **6** does not react readily at room

Table 1. Catalytic Metathesis Reactions Initiated by **6** in C_6D_6 at 22 °C

olefin	6 (equiv)	$\text{B}(\text{C}_6\text{F}_5)_3$	product
cyclooctene	0.05	0.1	>99% poly(COE)
1-decene ^a	0.01	0.02	20m ; 57%; 68/32 ^b 18h ; 84%; 55/45
DCMNBD	0.01	none	18h ; 95%; 81/19
	0.01	0.02	10m ; >99%; 98/2 ^c
<i>rac</i> -DCMNBE	0.01	0.02	1h ; >99%; 98/2 ^d

^aOpen vial. ^bZ/E ratio. ^c*cis,syndiotactic*; $M_w = 61500$ in CHCl_3 vs PEG; $M_w/M_n = 2.76$. ^d*cis,syndiotactic,alt*; $M_w = 476000$ in CHCl_3 vs PEG; $M_w/M_n = 1.80$.

temperature with cyclooctene, 1-decene, or ethylene, it will react slowly with 5,6-dicarbomethoxynorbornadiene (DCMNBD) and 5,6-dicarbomethoxynorbornene (DCMNBE) (Table 1). However, when two equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ per Mo were added along with the olefin, 1-decene was converted into 9-octadecene (in an open vial), and cyclooctene (DCMNBD) and *rac*-DCMNBE were polymerized readily at room temperature. (An analogous experiment involving ethylene and $\text{B}(\text{C}_6\text{F}_5)_3$ led only to slow decomposition of **6**.) Both *E*- and *Z*-9-octadecene are formed from 1-decene, in part through secondary isomerization of *Z* to *E* with time.

It is important to note that the structure of poly(DCMNBD) is >97% *cis,syndiotactic*, whereas poly(DCMNBE) is >97%

cis,syndiotactic,alt (a *cis,syndiotactic* structure with a backbone that contains alternating enantiomer units; the errors are proposed to be *trans, isotactic* dyads formed from the same²⁰ or different enantiomers). These polymers have characteristic carbon and proton NMR spectra (Figure 4 and SI) and are

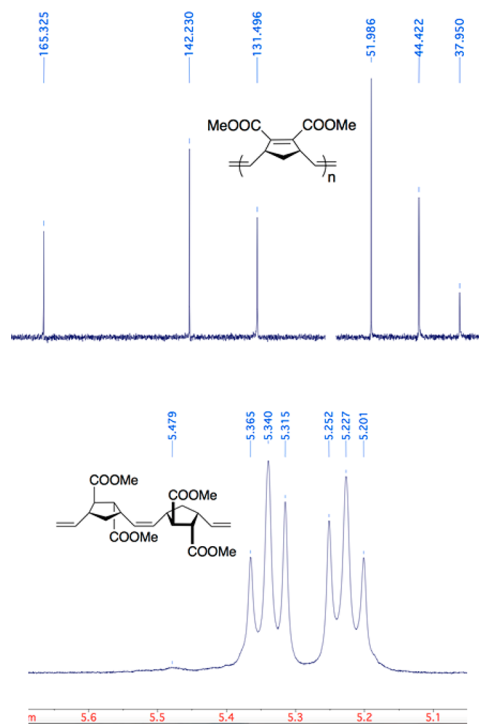


Figure 4. Carbon NMR spectrum of poly(DCMNBD) (top) and the olefinic region of the proton NMR spectrum of poly(DCMNBE) (bottom).

essentially identical to analogous polymers made from monoaryloxide pyrrolide Mo or W initiators.^{9c,d,21} Molecular weight studies of the polymers, as well as NMR studies, suggest that initiation is not complete before all monomer is consumed. Therefore, we can be relatively certain that (i) loss of PMe_3 is the slow step in initiation of metathesis, (ii) the **14e** core of the oxo alkylidene complex initiates the polymerization reaction, and (iii) $\text{B}(\text{C}_6\text{F}_5)_3$ scavenges free PMe_3 . We also propose that $\text{B}(\text{C}_6\text{F}_5)_3$ coordinates reversibly to the oxo ligand in (phosphine-free) **3** and analogous alkylidenes that are formed. The proposed binding of $\text{B}(\text{C}_6\text{F}_5)_3$ is consistent with the isolation of $\text{B}(\text{C}_6\text{F}_5)_3$ adducts of oxo alkylidene complexes that are significantly more reactive toward olefins than the boron-free initiators.^{9d} In at least one case, the boron-activated initiator produced a *more* highly structured polymer than the parent initiator.^{9d} We also find here that the poly(DCMNBD) formed (much more slowly) in the absence of $\text{B}(\text{C}_6\text{F}_5)_3$ is less regular (81/19) than that formed in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ (98/2; Table 1).

In closing, we have shown that molybdenum oxo alkylidene complexes can be prepared in a controlled fashion through addition of water to an alkylidyne complex. The highest yields are found when **4(dme)** forms rapidly and does not react further with water before the reaction between **2** and water is complete. These studies offer a rare view of important details in reactions between water and high oxidation-state alkylidene^{5a} or alkylidyne complexes.²² We do not yet know whether reactions of the type that yield **4(dme)** can be controlled to the same degree if the alkylidene ligand is not an *ortho*-methoxy benzyliidene. Finally,

we have shown that Mo oxo alkylidene complexes are capable of promoting stereoselective ring-opening metathesis reactions. We are now confident that other catalytically active molybdenum oxo alkylidene complexes can be prepared and look forward to exploring their reactions with olefins in detail.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.8b00499](https://doi.org/10.1021/jacs.8b00499).

X-ray crystallographic files of **3**(PPhMe₂) (CIF), **4**(dme) (CIF), and **6** (CIF)

Details of the synthesis and NMR and spectral data for all compounds and details of the metathesis experiments (PDF)

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Notes

The authors declare no competing financial interest.

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