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

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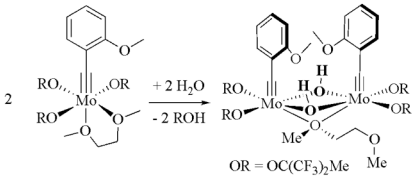
Abstract

Addition of one equiv of water to Mo(CAr)[OCMe$(CF_3)_2$]$_3$(1,2-dimethoxyethane) (**2**, Ar = *o*-(OMe)C_6H_4) in the presence of $PPhMe_2$ leads to formation of Mo(O)(CHAr)[OCMe$(CF_3)_2$]$_2$($PPhMe_2$) (**3(PPhMe$_2$)**) in 34% yield. Addition of one equiv of water alone to **2** produces the dimeric alkylidyne hydroxide complex, {Mo(CAr)[OCMe$(CF_3)_2$]$_2$(μ-OH)}$_2$(dme) (**4(dme)**) in which each bridging hydroxide proton points toward an oxygen atom in an arylmethoxy group. Addition of PMe_3 to **4(dme)** gives the alkylidene oxo complex, (**3(PMe$_3$)**), an analog of **3(PPhMe$_2$)** (95% conversion, 66% isolated). Treatment of **3(PMe$_3$)** with two equiv of HCl gave Mo(O)(CHAr)Cl_2(PMe_3) (**5**), which upon addition of LiO-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (LiOHIPT) gave Mo(O)(CHAr)(OHIPT)Cl(PMe_3) (**6**). Compound **6** in the presence of B$(C_6F_5)_3$ 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(PPhMe$_2$)**, **4(dme)**, and **6**.

Graphical Abstract



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Supporting Information

Details of the synthesis and NMR and spectral data for all compounds, details of the metathesis experiments, and X-ray crystallographic files for the three structures. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interests.

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 chemistry[4] because an imido ligand is less likely than an oxo ligand to bridge between metals[5] or to be attacked by an electrophile and removed from the metal.[6,7] A new approach to tungsten oxo alkylidenes[8] 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)($CHSiMe_3$)[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)$_3$]$^-$ ligand prevent facile initiation of olefin metathesis reactions, even upon "activating" Mo(O)($CHSiMe_3$)[NP(t-Bu)$_3$]$_2$ through addition of B(C_6F_5)$_3$ to the oxo ligand.[9b,11] (Addition of B(C_6F_5)$_3$ 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 J. H. Wengrovius[12] noted in his Ph.D. thesis that W(C-t-Bu)(PMe_3)$_3Cl_3$ reacts with one equivalent of water in CH_2Cl_2 to give W(O)(CH-t-Bu)(PMe_3)$_2Cl_2$ and Me_3PHCl 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 C_6H_4(*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 $PPhMe_2$ led to **3(PPhMe$_2$)** in 34% yield. An X-ray study of **3(PPhMe$_2$)** (Figure 1) confirmed that the alkylidene is orientated in the *anti* manner ($J_{CH\alpha}$ = 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 PMe_3, PEt_3, P(*i*-Pr)$_3$, and PPh_2Me in the reaction between **2** and water revealed that a product analogous to **3(PPhMe$_2$)** is formed only in the case of PMe_3 (**3(PMe$_3$)**, 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 dme) in the absence of any phosphine at −20°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 minutes, 54% in 19h, at 22°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 alkylidyne complex (Figure 2; Mo1-Mo2 = 3.2164(2) Å). The benzylidyne ligands are tipped slightly toward the bridging hydroxides (Mo2-C21-C22 = 167.33(7)°; Mo1-C11-C12 = 168.57(7)°) and turned so that the methoxy oxygen in each benzylidyne ligand is situated over the hydroxy protons (H7 and H8), which were located. The O(methoxy)···O(hydroxy) distances are 2.904 Å and 2.814 Å, the OH···O distances are 2.134 Å and 2.026 Å, and the O-H···O angles are 163.75° and 158.82°. IR data (ν_{OH} = 3482 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(PEt_3)$_2$(*o*-$MeOC_6H_4$)(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 CD_2Cl_2 in the presence of thirteen equiv of diethyl ether shows it to consist of a mixture of **4(dme)** (δ_{OH} = 9.30 ppm) and **4(ether)** (δ_{OH} = 9.24 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 $PPhMe_2$ in pentane gave **3($PPhMe_2$)** in ~30% yield, approximately the same as in the reaction between **2** and water in the presence of $PPhMe_2$ (34% yield). However, a reaction between **4(dme)** and ten equivalents of PMe_3 (five equivalents of PMe_3 per Mo; Scheme 2) gave **3(PMe_3)** in 95% yield (by proton NMR) and **3(PMe_3)** was isolated in 66% yield. The key mechanistic question is exactly how does a given hydroxy proton find its way to one or the other alkylidyne 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 benzylidyne carbon atom. Although we cannot exclude the possibility that Me_3PH^+ 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 PMe_3 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(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*-PrC_6H_2)$_2$$C_6H_3$). An X-ray study revealed **6** to have the structure shown in Figure 3. The bond distances are in the range

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(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 analog, 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 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 B(C_6F_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 B(C_6F_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 and a backbone that contains alternating enantiomer units; the errors are proposed to be *trans,isotactic* dyads formed from the same,[20] or different enantiomers). These polymers have characteristic carbon and proton NMR spectra (Figure 4 and SI) and are essentially identical to analogous polymers made from monoaryloxide pyrrolide Mo or W initiators.[9c,9d,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) B(C_6F_5)$_3$ scavenges free PMe_3. We also propose that B(C_6F_5)$_3$ coordinates reversibly to the oxo ligand in (phosphine-free) **3** and analogous alkylidenes that are formed. The proposed binding of B(C_6F_5)$_3$ is consistent with the isolation of B(C_6F_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 than the parent initiator.[9d] We also find here that the poly(DCMNBD) formed (much more slowly) in the absence of B(C_6F_5)$_3$ is less regular (81/19) than that formed in the presence of B(C_6F_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 benzylidene. 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.

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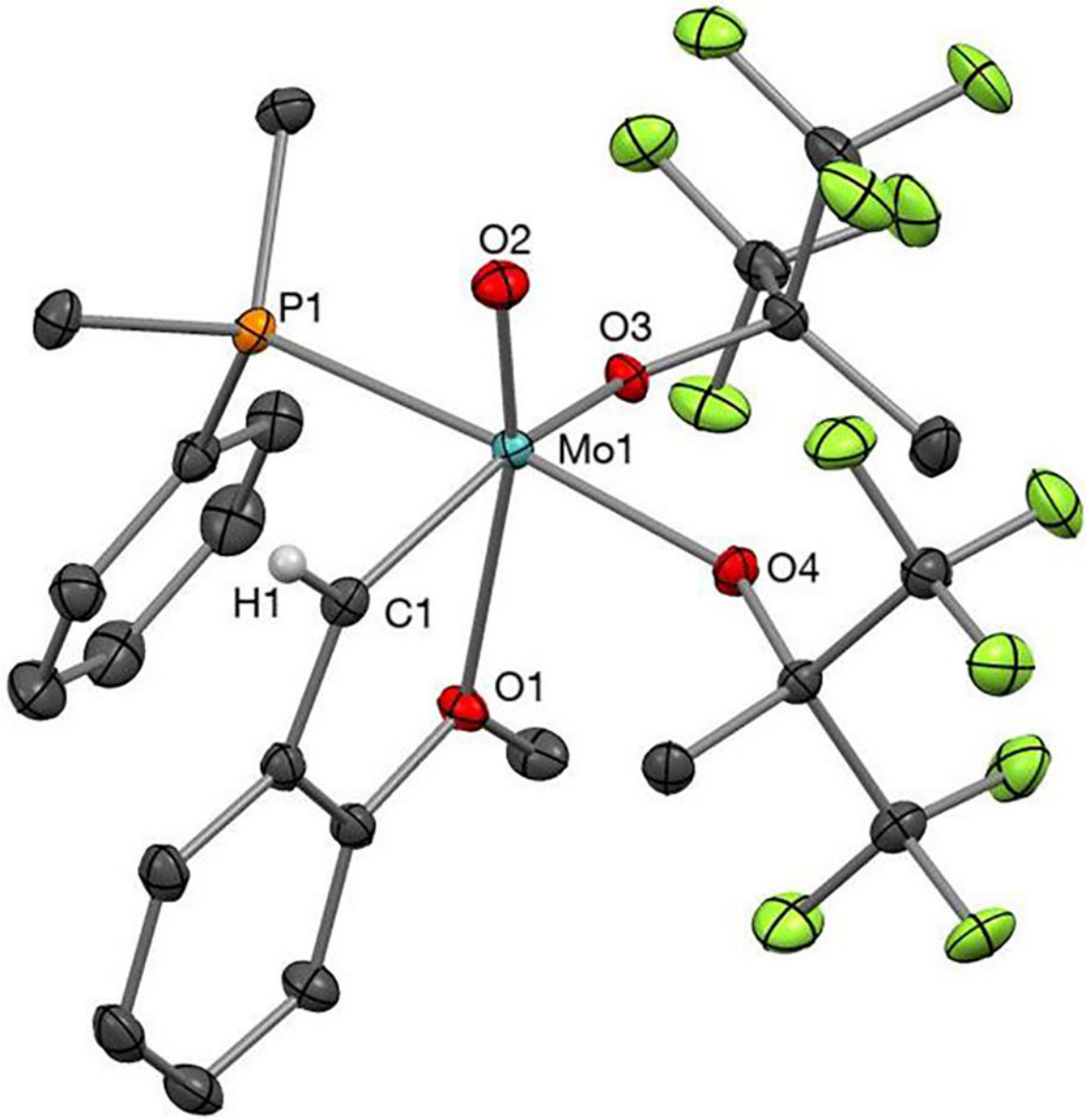


Figure 1.
A drawing of the X-ray structure of **3(PPhMe$_2$)**.

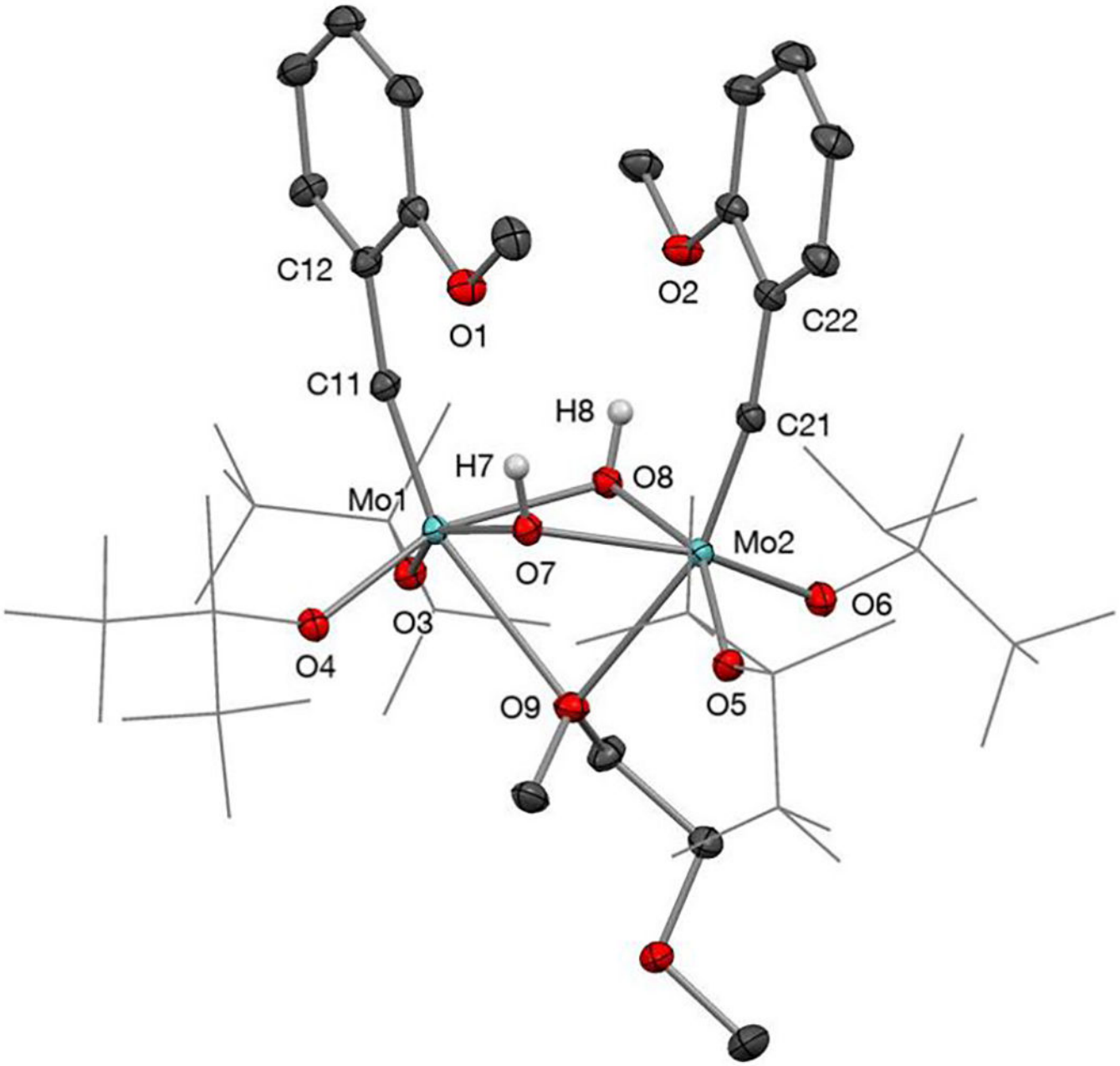


Figure 2.
A drawing of the X-ray structure of **4(dme)**.

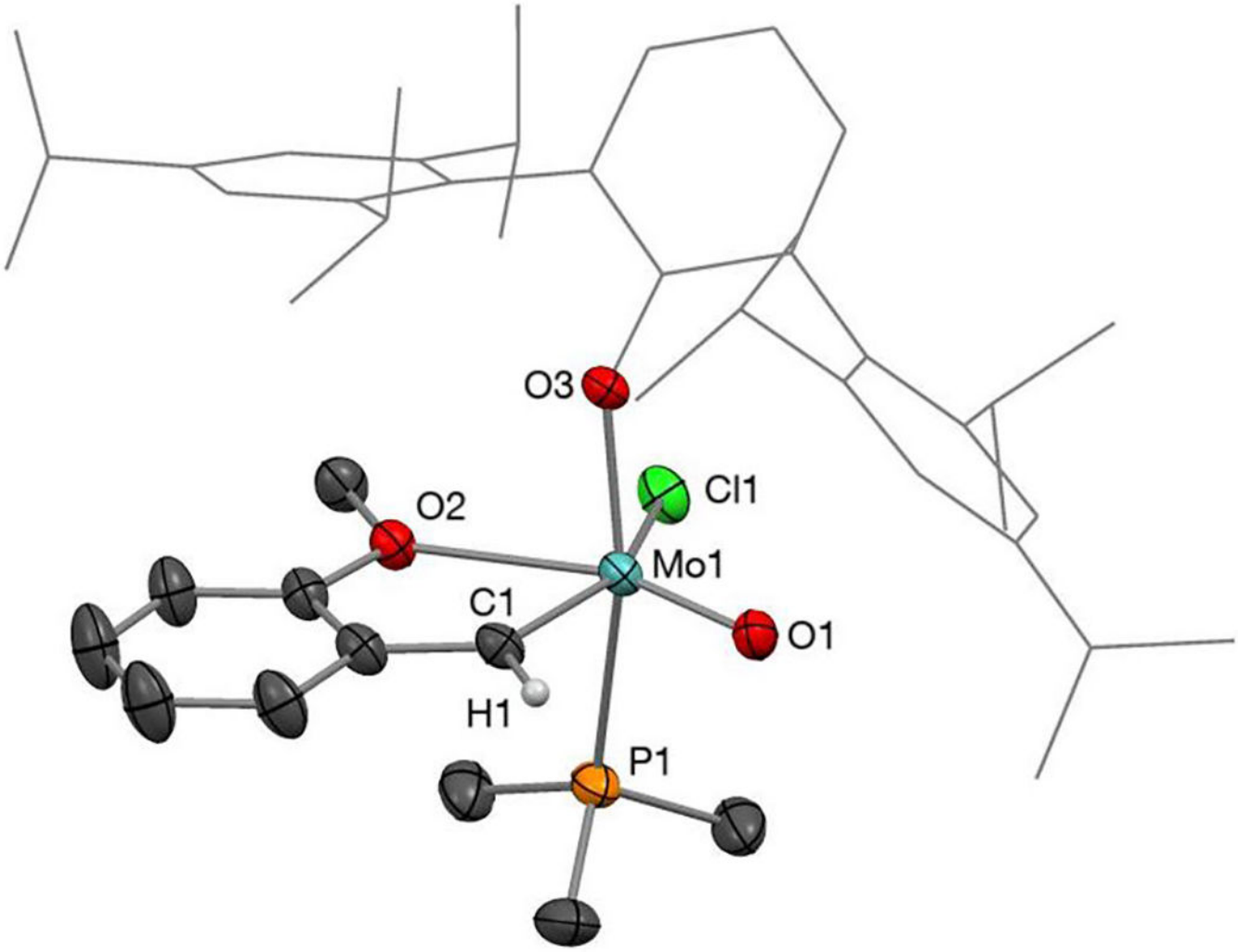


Figure 3.
A drawing of the X-ray structure of **6**.

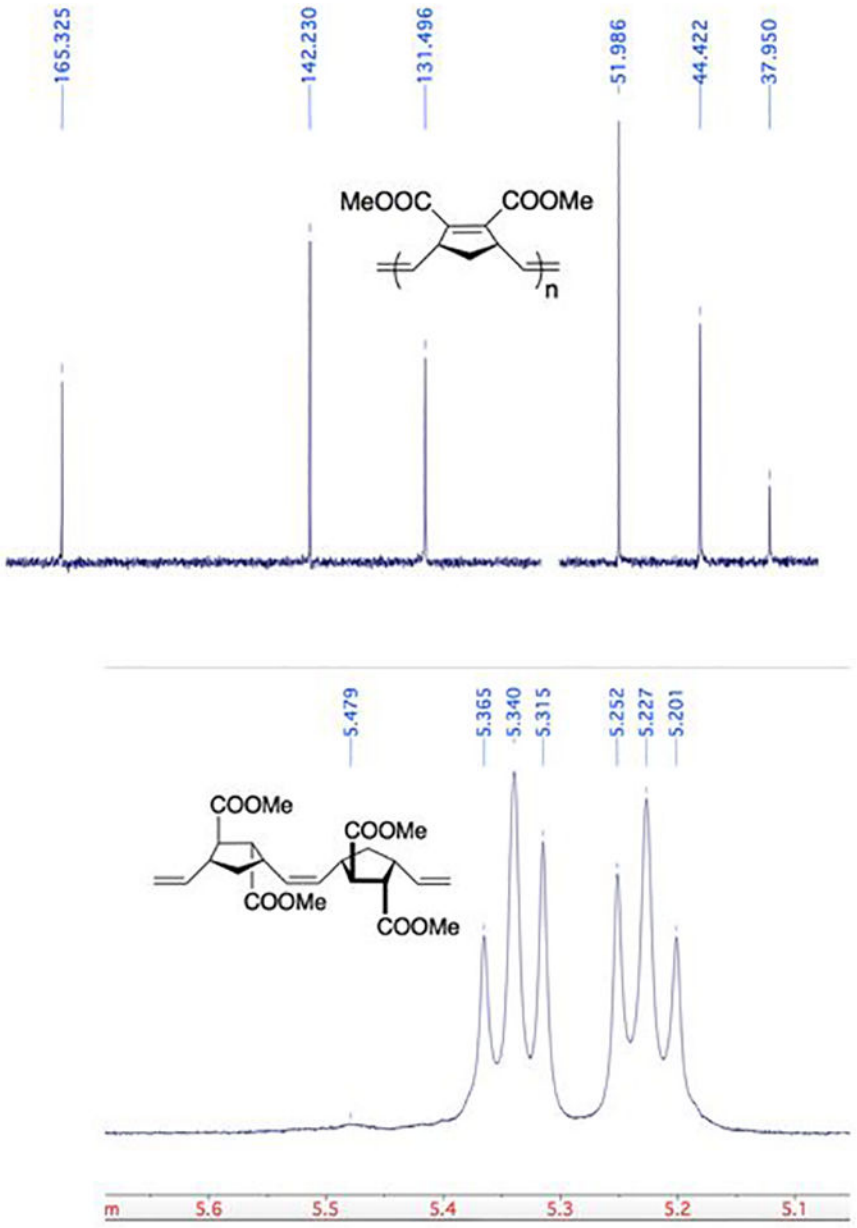
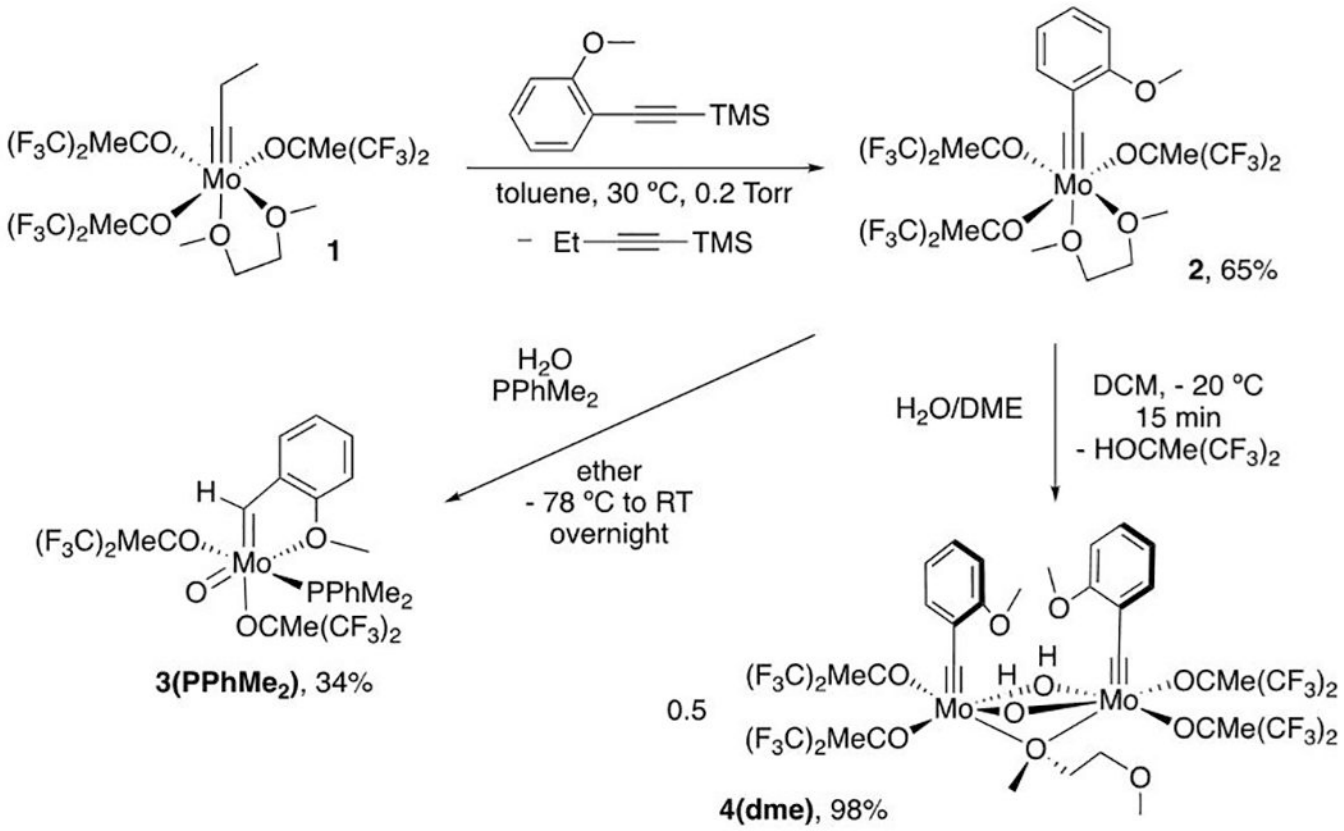
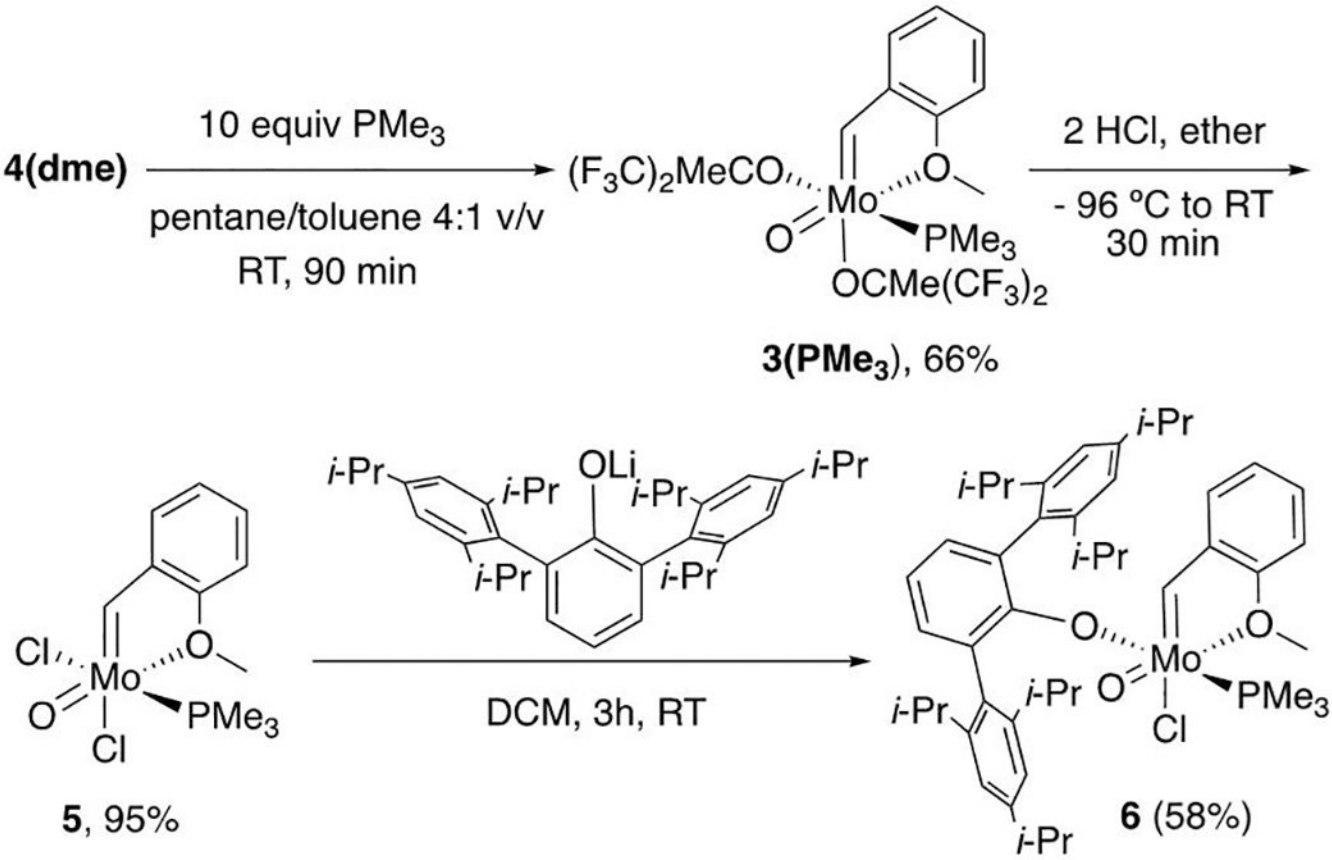


Figure 4.

The carbon NMR spectrum of poly(DCMNBD) (top) and the olefinic region of the proton NMR spectrum of poly(DCMNBE) (bottom).



Scheme 1.



Scheme 2.

Table 1.

Catalytic metathesis reactions initiated by **6** in C_6D_6 at 22°C.

Olefin	6 (equiv)	$B(C_6F_5)_3$	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]
rac-DCMNBE	0.01	0.02	1h;>99%;98/2[d]

[a] Open vial.

[b] *Z/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.