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Syntheses of Molybdenum Oxo Benzylidene Complexes

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Abstract

The reaction between $\text{Mo}(\text{O})(\text{CHAr}_o)(\text{OR}_{\text{F6}})_2(\text{PMe}_3)$ (Ar_o = *ortho*-methoxyphenyl, OR_{F6} = $\text{OCMe}(\text{CF}_3)_2$) and two equivalents of LiOHMT (OHMT = $\text{O}-2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$) leads to $\text{Mo}(\text{O})(\text{CHAr}_o)(\text{OHMT})_2$, an X-ray structure of which shows it to be a trigonal bipyramidal *anti* benzylidene complex in which the *o*-methoxy oxygen is coordinated to the metal *trans* to the apical oxo ligand. Addition of one equivalent of water (in THF) to the benzylidyne complex, $\text{Mo}(\text{CAr}_p)(\text{OR})_3(\text{THF})_2$ (Ar_p = *para*-methoxyphenyl, OR = OR_{F6} or $\text{OC}(\text{CF}_3)_3$ (OR_{F9})) leads to formation of $\{\text{Mo}(\text{CAr}_p)(\text{OR})_2(\mu\text{-OH})(\text{THF})\}_2(\mu\text{-THF})$ complexes. Addition of one equivalent of a phosphine (L) to $\text{Mo}(\text{CAr}_p)(\text{OR}_{\text{F9}})_3(\text{THF})_2$ in THF, followed by addition of one equivalent of water, all at room temperature, yields $\text{Mo}(\text{O})(\text{CHAr}_p)(\text{OR}_{\text{F9}})_2(\text{L})$ complexes in good yields for several phosphines (*e.g.*, PMe_2Ph (69% by NMR), PMePh_2 (59%), PEt_3 (69%), or $\text{P}(i\text{-Pr})_3$ (65%)). The reaction between $\text{Mo}(\text{O})(\text{CHAr}_p)(\text{OR}_{\text{F9}})_2(\text{PEt}_3)$ and two equivalents of LiOHMT proceeds smoothly at 90 °C in toluene to give $\text{Mo}(\text{O})(\text{CHAr}_p)(\text{OHMT})_2$, a four-coordinate *syn* alkylidene complex. $\text{Mo}(\text{O})(\text{CHAr}_p)(\text{OHMT})_2$ reacts with ethylene (1 atm in C_6D_6) to give (in solution) a mixture of $\text{Mo}(\text{O})(\text{CHAr}_p)(\text{OHMT})_2$, $\text{Mo}(\text{O})(\text{CH}_2)(\text{OHMT})_2$, and an unsubstituted square pyramidal metallacyclobutane complex, $\text{Mo}(\text{O})(\text{CH}_2\text{CH}_2\text{CH}_2)(\text{OHMT})_2$, along with ethylene and $\text{Ar}_p\text{CH}=\text{CH}_2$. $\text{Mo}(\text{O})(\text{CHAr}_p)(\text{OHMT})_2$ also reacts with 2,3-dicarbomethoxynorbornadiene to yield *syn* and *anti* isomers of the “first-insertion” products that contain a *cis* C=C bond.

The neopentylidyne ligand in $(t\text{-BuCH}_2)_3\text{M}\equiv\text{C}-t\text{-Bu}$ ($\text{M} = \text{W}^1$ or Mo^2) complexes is formed through what amounts to an intramolecular deprotonation of an α carbon atom in one alkyl ligand by another in some multialkyl intermediate to give an alkylidene first,³ followed by a

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Supporting Information

Experimental details of the syntheses of all compounds, NMR and spectral data, details of the metathesis experiments, and X-ray crystallographic files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes

CCDC 1865865–1865868 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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second (more facile) α deprotonation of that alkylidene by an alkyl to give the alkylidyne.⁴ Synthesis of $M(C-t-Bu)(1,2\text{-dimethoxyethane})Cl_3$ and $M(C-t-Bu)(OR)_3$ complexes (OR is a sterically demanding alkoxide or aryloxy) and the demonstration that the latter are initiators for catalytic *alkyne* metathesis⁵ led to the development of four-coordinate *alkene* metathesis initiators of the type $M(NR')(CHR')(OR)_2$ ($M = Mo$ or W).^{6,7} Synthetic routes to imido alkylidene complexes of Mo and W are based on a single α hydrogen abstraction/deprotonation reaction in a dineopentyl or dineophyl complex.⁸ Syntheses of oxo alkylidenes, which have been proposed to be the type of alkene metathesis catalysts present in “classical” heterogeneous catalyst systems,⁹ by analogous methods have been more challenging. Tungsten oxo alkylidene complexes were prepared through α hydrogen abstraction in tungsten dialkyls in 2012,¹⁰ but syntheses of molybdenum oxo alkylidene complexes that are active for metathesis of olefins have remained elusive.¹¹ Recently we began to explore the synthesis of Mo oxo alkylidene complexes through addition of water to alkylidyne complexes.^{7,12}

Addition of one equiv of water to $Mo(CAr_o)(OR_{F6})_3(dme)$ ($Ar_o = ortho\text{-methoxyphenyl}$) gives the dimeric benzylidyne hydroxo complex, $\{Mo(CAr_o)(OR_{F6})_2(\mu-OH)\}_2(\mu-dme)$ in which each bridging hydroxo proton is hydrogen-bonded to the *ortho* methoxy oxygen in the *o*-methoxybenzylidyne ligand. (This is a rare example of a controlled hydrolysis of a high oxidation state alkylidene or alkylidyne.^{13,14}) Addition of PMe_3 to $\{Mo(CAr_o)(OR_{F6})_2(\mu-OH)\}_2(\mu-dme)$ led to formation of $Mo(O)(CHAr_o)(OR_{F6})_2(PMe_3)$, from which $Mo(O)(CHAr_o)Cl_2(PMe_3)$ and $Mo(O)(CHAr_o)(OHIPT)Cl(PMe_3)$ ($OHIPT = O\text{-}2,6\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3$ ¹⁵) were prepared. In the presence of $B(C_6F_5)_3$ $Mo(O)(CHAr_o)(OHIPT)Cl(PMe_3)$ was shown to be active for the stereoselective ring-opening metathesis polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNBD) and *rac*-2,3-dicarbomethoxy-5-norbornene (DCMNBE), and the homocoupling of 1-decene to 9-octadecene, consistent with analogous reactions that use tungsten-based initiators¹⁶ and with removal of PMe_3 to form active metathesis initiators. Important questions are whether an *ortho*-methoxy group in the benzylidyne and benzylidene ligands is required for a controlled reaction involving water and an alkylidyne complex and whether phosphine-free complexes that are active for olefin metathesis can be prepared and isolated. Some answers to these questions are provided in this communication.

The synthesis and stability of $W(O)(CH-t-Bu)(OHMT)_2$ ($OHMT = O\text{-}2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$ or hexamethylterphenoxide¹⁷)^{10a} suggested that the phosphine-free target should be $Mo(O)(CHAr_o)(OHMT)_2$ (**1- Ar_o**); it was prepared from $Mo(O)(CHAr_o)(OR_{F6})_2(PMe_3)$ as shown in eq 1. Trimethylphosphine is lost in the process as a consequence of steric hindrance overall in combination with binding of the methoxide oxygen in the Ar_o group in the *anti* alkylidene to the metal *trans* to the oxo ligand, as shown through an X-ray study (Fig 1; see SI). The τ value¹⁸ (0.78) suggests that the configuration at the metal is closest to a trigonal bipyramid ($O2-Mo1-O1 = 166.27(7)^\circ$). Alkylidene proton resonances were observed in the initial proton NMR spectrum of **1- Ar_o** at 11.92 ppm for the *anti* isomer (97%, $J_{CH} = 156$ Hz), the isomer found in the solid state (Fig 1), and at 12.02 ppm for the *syn* isomer ($J_{CH} = 134$ Hz), in which the alkylidene has rotated¹⁹ by 180° and

the methoxide is not bound to the metal. After 1 h at 50 °C an 85:15 equilibrium ratio of *anti* to *syn* isomers was observed.

(1)

Preliminary studies showed that the rate of reaction of **1-Ar_o** with ethylene is slow, perhaps because the lower energy “methoxy-bound” *anti* form only slowly converts to the more reactive *syn* form. We therefore turned to a synthesis of the *p*-methoxybenzylidene analog where intramolecular binding of the methoxy oxygen is not possible.

The *para*-methoxybenzylidyne complex, Mo(CAr_p)(dme)Br₃ was prepared by the “low oxidation state” procedure.²⁰ From it Mo(CAr_p)(OR_{F6})₃(dme)²¹ and Mo(CAr_p)(OR_{F6})₃(THF)₂²² were prepared without complications. Addition of one equivalent of water (in THF, diethyl ether, or dichloromethane) to Mo(CAr_p)(OR_{F6})₃(THF)₂ led to the formation of {Mo(CAr_p)(OR_{F6})₂(μ-OH)}₂(THF)₃ (**2-Ar_pF₆**) in good yield (eq 2). It was crystallized from a mixture of pentane and CH₂Cl₂ at –40 °C in the presence of several equivalents of THF and isolated in 70% yield as pale red crystals. Similar reactions starting with Mo(CAr_p)(OR_{F6})₃(dme) and one equivalent of water (in THF) also led to **2-Ar_pF₆**, but in poor yield (~10%), while addition of water in dme to Mo(CAr_p)(OR_{F6})₃(dme) did not lead to an isolable benzylidyne hydroxo complex. Dme appears to be detrimental and THF beneficial for formation of benzylidyne hydroxo complexes in these circumstances.

(2)

An X-ray study of **2-Ar_pF₆** (Fig 2) shows its structure to be analogous to that of previously reported¹² {Mo(CAr_o)(OR_{F6})₂(μ-OH)}₂(μ-dme) with one of the THFs bridging the two Mo centers and one THF hydrogen-bonded to each of the two bridging hydroxos. The OH...O angles and O...O distances are consistent with a “classical” hydrogen bond between the bridging hydroxo protons and THF oxygens.²³ The hydroxo proton resonance in **2-Ar_pF₆** is found at 6.60 ppm in the proton NMR spectrum in CD₂Cl₂ (*cf.* 9.30 ppm for the hydroxo protons in {Mo(CAr_o)(OR_{F6})₂(μ-OH)}₂(μ-dme)). The Mo-O distance to the bridging THF is 2.485(2) Å. The Mo-C-C_{ipso} angles are 179.4(2)°, in contrast to 168.57(7)° and 167.33(7)° in {Mo(CAr_o)(OR_{F6})₂(μ-OH)}₂(μ-dme), which result from the hydroxo protons being hydrogen bonded to the *o*-methoxy oxygens in the Ar_o group instead of to THF, as found in **2-Ar_pF₆**. Other distances and angles are not unusual (see SI). In solution, proton NMR resonances for the bridging THF are distinct from those for the hydrogen-bonded THFs or THF in solution. The hydrogen-bonded THFs are readily lost from solid samples, especially *in vacuo*, to give {Mo(CAr_p)(OR_{F6})₂(μ-OH)}₂(μ-THF), and exchange rapidly on the NMR scale with free THF in solution, as shown through proton NMR studies. Addition of dioxane to an NMR sample of {Mo(CAr_p)(OR_{F6})₂(μ-OH)}₂(μ-THF) led to formation of a mixture of the μ-THF (δ_{OH} at 6.63 ppm) and μ-dioxane (δ_{OH} at 6.51 ppm) complexes.

Addition of one equivalent of water (in THF) to Mo(CAr_p)(OR_{F9})₃(THF)₂ in CH₂Cl₂ led to formation of {Mo(CAr_p)(OR_{F9})₂(μ-OH)}₂(μ-THF), which could be isolated in 43 % yield as lime-green crystals; in the presence of additional THF it crystallizes as {Mo(CAr_p)(OR_{F9})₂(μ-OH)(THF)}₂(μ-THF) (**2-Ar_pF₉**). An X-ray structural study showed its structure to be entirely analogous to that for **2-Ar_pF₆** (see SI for details). The two molecules of hydrogen-bonded THF in **2-Ar_pF₉** again are lost readily from solid samples, especially *in vacuo*. The μ-OH resonance is found at 8.21 ppm in **2-Ar_pF₉** in CD₂Cl₂ (*cf.* 6.60 ppm in **2-Ar_pF₆**).

Reactions between **2-Ar_pF₆** or **2-Ar_pF₉** and PMe₃ or PEt₃ (L) do *not* yield Mo(O)(CHAr_p)(OR)₂(L) complexes readily and in high yield. However, addition of one equivalent of L to Mo(CAr_p)(OR_{F9})₃(THF)₂, followed by addition of one equivalent of water, *all at room temperature in THF*, yields Mo(O)(CHAr_p)(OR)₂(L) complexes (**3**) in good yields for several phosphines L (*e.g.*, PMe₂Ph (69% by NMR), PMePh₂ (59%), PEt₃ (69%), or P(*i*-Pr)₃ (65%)). For example, Mo(O)(CHAr_p)(OR_{F9})₂(PEt₃) (**3-PEt₃**) can be prepared in this manner (eq 3). These results suggest that in most cases it is best to *avoid* formation of bis(μ-OH) dimers. We propose that THF discourages formation of a hydroxo benzyldiene dimer from monomeric Mo(CAr_p)(OR_{F9})₂(OH)(THF)_x (x unknown). We also propose that the hydroxo proton migrates to the benzyldiene α carbon intramolecularly in intermediate Mo(CAr_p)(OR_{F9})₂(OH)(THF)_x to give Mo(O)(CHAr_p)(OR_{F9})₂(THF)_x, which is then trapped by L to give Mo(O)(CHAr_p)(OR_{F9})₂(L) complexes. Phosphines can also bind to Mo in Mo(CAr_p)(OR_{F9})₂(OH)(THF)_x and help prevent formation of μ-OH products and promote (perhaps along with THF itself) migration of the proton from O to C. Formation of OR_{F6} analogs of **3** at room temperature in THF does not appear to be as successful, most likely because the migrating proton is less acidic in OR_{F6} hydroxo benzyldiene complexes. Studies that address multiple mechanistic issues are ongoing.

(3)

Mo(O)(CHAr_p)(OR_{F9})₂(PEt₃) (**3-PEt₃**) was chosen to proceed further toward the goal of preparing a four-coordinate complex. The reaction between **3-PEt₃** and two equivalents of LiOHMT proceeds smoothly at 90 °C in toluene over a period of 1.5 h to give Mo(O)(CHAr_p)(OHMT)₂ (**1-Ar_p**) which could be isolated as plum-purple needles (eq 4). The alkylidene proton resonance is found at 11.20 ppm (in C₆D₆) with *J*_{CH} = 130 Hz, consistent with the alkylidene being in the *syn* conformation. The corresponding *anti* isomer was not found in solution even upon heating a sample of **1-Ar_p** at 100 °C, which suggests that coordination of an *ortho* methoxide in **1-Ar_o** (Fig 1) stabilizes the *anti* form. The OHMT ligands in the proton NMR spectrum at 22 °C are equivalent on the NMR time scale through mirror symmetry. The purple color of **1-Ar_p** (λ_{max} = 532 nm with ε₅₃₂ ~ 400) is unusual for a “d⁰” complex of this general type. We propose that the purple color arises from a weak LMCT transition that involves the *p*-methoxybenzylidene ligand. Compound **1-Ar_p** also was prepared from **3-PMePh₂** in 66% yield on a 500 mg scale at 70 °C in 3.5 h.

(4)

An X-ray structural study of **1-Ar_p** (Fig 3) reveals that the OHMT terphenyl groups are roughly “interlocked,” as they are in W(O)(CH₂)(OHMT)₂,^{10b} although they rotate readily around the Mo-O bonds on the NMR time scale in solution at 22 °C. The relevant distances and angles are similar to those in **1-Ar_o** (see Fig 1 and SI). Together the two OHMT ligands prevent PEt₃ or PMePh₂ from remaining bound to the metal in the final product and also

provide a significant degree of steric protection against bimolecular decomposition reactions.

Compound **1-Ar_p** reacts with ethylene (1 atm in C₆D₆ at 22 °C) to give an orange solution that contains a mixture of **1-Ar_p**, Mo(O)(CH₂)(OHMT)₂, and an unsubstituted metallacyclobutane complex, Mo(O)(CH₂CH₂CH₂)(OHMT)₂, along with Ar_pCH=CH₂, and ethylene, according to proton NMR studies. At a molybdenum concentration of 17 mM in C₆D₆, the ratio of Mo=CHAr_p : Mo=CH₂ : Mo(C₃H₆) : Ar_pCH=CH₂ is 57:5:38:43 (43% conversion) after 1.5 h. The 1:1:2:2 pattern of the four metallacycle proton resonances in Mo(O)(CH₂CH₂CH₂)(OHMT)₂ at 2.92, 2.39, 1.68, and 0.45 ppm suggest that it has a square pyramidal structure.²⁴ So far, efforts to isolate Mo(O)(CH₂CH₂CH₂)(OHMT)₂, an analog of isolable W(O)(CH₂CH₂CH₂)(OHMT)₂,^{10b} have not been successful.

Compound **1-Ar_p** does not react readily with several equivalents of *Z*-5-decene at 22°C. It does react with 2,3-dicarbomethoxynorbornadiene (4 equiv) to yield a 17:1 mixture of *syn* (8 H_a at 11.63 ppm; eq 5) and *anti* isomers (not shown in eq 5) of the first insertion product, each of which contains a *cis* C=C bond.²⁵ (The yield (by NMR) is ~90%; see SI for details.) Both results are consistent with a relatively sterically demanding coordination sphere that limits access to an alkylidene, in contrast to Mo(O)(CHAr_o)(OHMT)₂Cl formed through removal of PMe₃ from Mo(O)(CHAr_o)(OHMT)₂(PMe₃)Cl, which forms polymers from 2,3-dicarbomethoxynorbornadiene readily.¹²

(5)

We conclude that the *o*-methoxy group is not required, either for forming a benzylidene ligand from a benzylidyne ligand or for stabilizing a bis(OHMT) oxo benzylidene complex. The most successful syntheses of oxo alkylidene complexes involve intramolecular α proton migrations from O to C, where C is the benzylidyne α carbon, and are most successful when OR is OR_{F9}, the solvent is THF, and a phosphine is available to trap the oxo benzylidene product and possibly help form it. Several phosphine adducts of molybdenum oxo benzylidene complexes are accessible via reactions between Mo(CAr_p)(OR)₃(THF)₂ complexes and water. We can now predict that other metathesis-active molybdenum oxo alkylidene complexes will be observed or isolated under the right circumstances, and look forward to comparing their metathesis reactions with those catalyzed by tungsten analogs.^{10,16}

Supplementary Material

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Figure 1.

A drawing of the structure of **1-Ar₀**; Mo1-C1 = 1.933(2) Å, Mo1-O2 = 1.6698(14) Å, Mo1-O1 = 2.4865(17) Å, Mo1-O3 = 1.915(2) Å, Mo1-O4 = 1.9295(15) Å.

Figure 2.
End view of the structure of **2-Ar_pF₆**.

Figure 3.

A drawing of the structure of **1-Ar_p**;

Mo1-C1 = 1.9004(13) Å, Mo1-O1 = 1.6803(10) Å, Mo1-O3 = 1.9064(9) Å, Mo1-O4 = 1.9113(9) Å, Mo1-C1-C_{ipso} = 137.42(10)°, Mo1-O3-C_{ipso} = 143.11(8)°, Mo1-O4-C_{ipso} = 127.58(8)°.