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Communication

Molybdenum Benzylidyne Complexes for Olefin Metathesis Reactions

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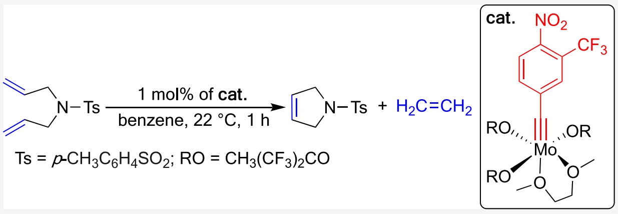
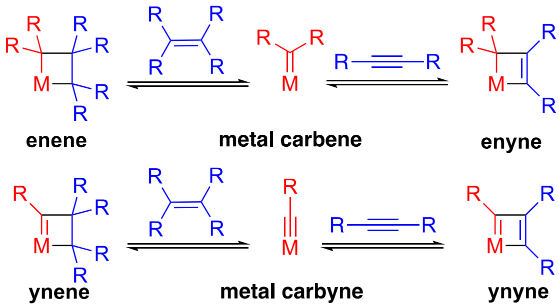
ABSTRACT: The molybdenum benzylidynes [$ArC{\equiv}Mo(OC(CF_3)_2CH_3)_3$(1,2-dimethoxyethane)], where Ar = Ph (**2a**), *p*-(OCH_3)C_6H_4 (**2b**), *p*-(CF_3)C_6H_4 (**2c**), *p*-(NO_2)C_6H_4 (**2d**), or 4-(NO_2)-3-(CF_3)C_6H_3 (**2e**), and [*p*-(NO_2)$C_6H_4C{\equiv}Mo(OC(CF_3)_2CH_3)_3$] (**2f**) catalyze the ring-closing metathesis (RCM) reaction of diallyl *N*-tosylamide (**3**) to produce 1-tosyl-2,5-dihydro-1*H*-pyrrole (**4**) and ethylene. The scope of RCM catalytic activity of **2e**, cross-metathesis of 1-hexene, and ring-opening metathesis polymerization of cyclooctene were explored. The X-ray crystal structure of **2e** was determined. Variable-temperature ^{1}H NMR spectra revealed the formation of intermediates during the reaction of **3** with **2f** and the reforming of **2f** after completion of the reaction. The use of ^{13}C-labeled Mo benzylidyne did not show transfer of the carbon atom next to Mo to any of the products.



■ INTRODUCTION

Catalytic transformations based on the [2 + 2] cycloaddition reaction between a metal carbyne and an alkene (ynene)[1] represent an underdeveloped reaction class among olefin (enene),[2−4] alkyne (ynyne),[5−8] and enyne[9] metathesis transformations (Scheme 1). The first example of metathesis involving alkenes catalyzed by a well-defined tungsten alkylidyne complex, [$Cl_3(dme)W{\equiv}C{-}CMe_3$], was reported in 1986 by Weiss.[10,11] Although this complex successfully polymerized cyclopentene and catalyzed the cross-metathesis of 1-octene, the structure of the active species was not elucidated. Traces of water in the reaction mixture should be considered since alkylidyne complexes can react with water to form oxoalkylidenes, which are active catalysts for olefin metathesis.[12,13] Three decades after Weiss' discovery, Veige showed that a trianionic pincer alkylidyne complex, $[OCO]^{3-}$W, can reversibly react with ethylene to form metallacyclobutene, with the structure of the latter confirmed spectroscopically.[1] Additionally, a catalytic reaction based on ynene [2 + 2] cycloaddition was used to prepare cyclic cis-syndiotactic polynorbornenes.

Scheme 1. Four Types of [2 + 2] Cycloaddition Reactions Involving Metal Carbene and Carbyne Complexes



A similar trianionic pincer molybdenum benzylidyne complex, $[OCO]^{3-}$Mo, was synthesized, but its reactivity toward alkenes was not discussed.[14] Generally, Mo carbyne complexes do not react with alkenes. This orthogonality has been used in the total synthesis of many natural products containing both alkene and alkyne moieties, where only alkyne metathesis occurred.[15−22]

Recently, Fischer found that electron-donating or -withdrawing substituents on the benzylidyne [*p*-R-$C_6H_4C{\equiv}Mo(OC(CF_3)_2CH_3)_3$] can significantly affect the initiating step in ring-opening alkyne metathesis polymerization (ROAMP).[23] Density functional theory calculations have shown that the rate-determining step in the ROAMP initiation is associated with cycloelimination, where the carbon atom next to Mo at the benzylic α-position has a negative charge. Electron-withdrawing substituents stabilize the negative charge buildup in the transition state and as a result increase the rate of the initiation step. The rate of propagation is mostly unaffected by substituents on the initial benzylidyne, since a new benzylidyne forms after each catalytic cycle.

The observation by Fischer, the first spectroscopic evidence of a metallacyclobutene from Viege's lab, and the importance

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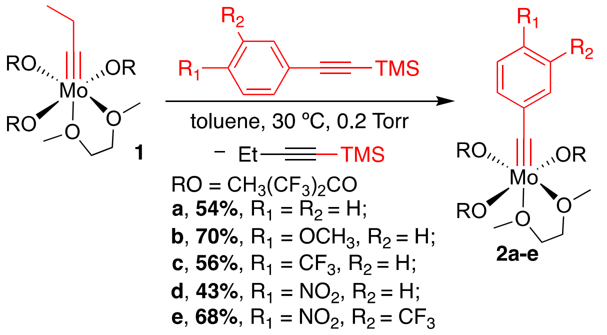
of Mo carbynes in modern organic and organometallic chemistry and catalysis[24−30] have led to our interest in examining the influence of the electron-donating or -withdrawing substituents on the benzylidyne [ArC≡Mo(OC(CF_3)$_2$$CH_3$)$_3$] with regard to its reactivity toward alkenes. We have now prepared Mo benzylidyne complexes that are reactive toward olefins. To our knowledge, we report the first examples of ring-closing metathesis (RCM), cross-metathesis (CM), and ring-opening metathesis polymerization (ROMP) of alkenes catalyzed by well-defined Mo benzylidyne complexes.

■ RESULTS AND DISCUSSION

The reaction between **1**[31,32] and $R_1R_2C_6H_3C{\equiv}C{-}TMS$ provided a series of benzylidyne complexes **2a−e** (Scheme 2) utilizing a method analogous to the published procedure.[12]

Scheme 2. Synthesis of Mo Benzylidyne Complexes 2a−e with Isolated Yields



During the synthesis, a limitation of the above reaction became apparent, as substrates containing the NO_2 group at the ortho position with respect to the alkyne did not lead to benzylidynes (see the Supporting Information for specific examples). The structures of **2a−d** were confirmed by ^{1}H NMR spectroscopy.[23]

Orange prisms of **2e** suitable for X-ray crystallography were obtained from a saturated toluene solution at −35 °C. The Mo center adopts a pseudo-octahedral geometry with Mo located 0.45 Å above the equatorial O_4 plane. The X-ray crystal structure of **2e** (Figure 1) confirms the presence of a C(1)≡Mo(1) triple bond with a bond length of 1.749(4) Å and a C(2)−C(1)−Mo(1) angle of 176.9(3)°. One 1,2-dimethoxyethane (DME) molecule is coordinated to the Mo center, with one of the O atoms located trans to the benzylidyne. The bond lengths of the Mo(1)−O(4) cis and Mo(1)−O(5) trans to the carbyne are 2.226(3) and 2.399(4) Å, respectively. Three hexafluoro-*tert*-butoxide ligands occupy meridional sites featuring Mo(1)−O(1), Mo(1)−O(2), and Mo(1)−O(3) distances of 1.946(3), 1.906(3), and 1.955(3) Å. The presence of the electron-withdrawing CF_3 group in **2e** has a small effect on the C(1)≡Mo(1) triple bond compared with **2d** (1.754(7) Å) and a C(2)−C(1)−Mo(1) angle of 174.8(6)°, but the changes in the bond lengths for Mo(1)−O(1), Mo(1)−O(2), and Mo(1)−O(3) are more pronounced (1.958(4), 1.922(4), and 1.952(5) Å, respectively) because of the weaker π-donating character of the carbyne in **2e**.[23]

Next, the metathesis activity of complexes **1** and **2a−e** in the RCM reaction with diallyl *N*-tosylamide (**3**) was explored (Table 1). The Mo benzylidyne complexes are active catalysts in the RCM reaction of **3**. The activity of the catalyst depends on the substituents on the benzylidyne. For instance, electron-withdrawing groups accelerate the reaction. Complex **2e** exhibits high RCM catalytic activity at 1 mol % (entry 7, Table 1), comparable to those of some Ru-[33] and W-based[34] alkylidene catalysts. The addition of water does not lead to the formation of a catalytically active Mo oxobenzylidene under the reaction conditions (entry 8, Table 1); instead, only decomposition of the catalyst was observed by ^{1}H NMR spectroscopy.

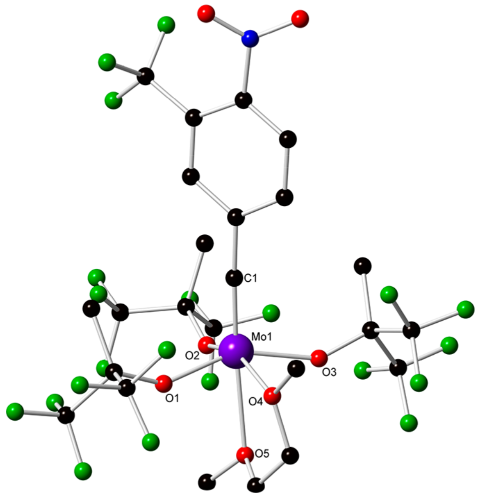
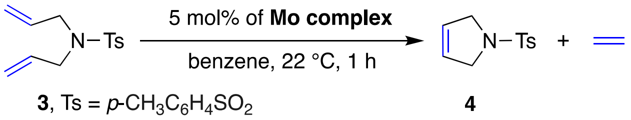


Figure 1. Drawing of the X-ray structure of **2e**.

Table 1. Metathesis Activity of Mo Carbynes toward 3[a]

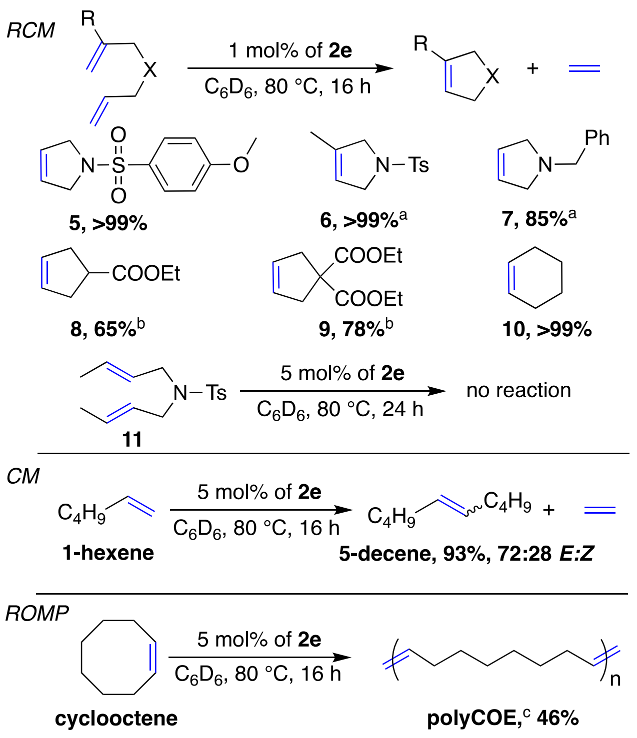


entry	Mo complex	conv. to **4** (%)[b]
1	**1**	<1
2	**2a**	61
3	**2b**	13
4	**2c**	64
5	**2d**	85
6	**2e**	>99
7	**2e**[c]	>99
8	**2e**[d]	<1

[a] 0.2 M **3**. [b] Determined by ^{1}H NMR spectroscopy. [c] 1 mol % **2e**. [d] 1 equiv of water was added.

We explored the scope of RCM and the metathesis activity of **2e** for CM of hexene-1 and ROMP of cyclooctene. The results are summarized in Scheme 3. Unlike **3**, the tested substrates require heating to speed up the reaction. The substrates used to make **5** and **7−9** contain basic groups that can compete with the alkene for coordination to Mo. Additionally, **9** can form a chelating complex through both oxygen atoms. The precursor for **6** is more hindered compared with **3**. Those factors can explain why heating is required to produce **5−9**. However, 1,7-octadiene (the substrate for **10**) and 1-hexene do not contain basic groups. Arguably, the reason for the higher activity of **2e** toward **3** is that the coordination of the sulfone group in **3** through one of its oxygen atoms[35] to DME-free **2e** (to be discussed later) facilitates the intramolecular coordination of the alkene group to Mo. However, this is not the case for internal olefins. Thus,

Scheme 3. Catalytic Metathesis Reactions Initiated by 2e[d]



[a] 5 mol % **2e**. [b] 24 h. [c] M_n = 109700 g/mol, M_w/M_n = 1.77 by GPC (THF vs polystyrene standards). [d] Conversions by ^1H NMR analysis are indicated.

ROMP of cyclooctene is slow at 80 °C in the presence of 5 mol % **2e**. The resulting polymer has a high molecular weight and polydispersity index based on gel-permeation chromatography, which suggests that the rate of the propagation is higher than that of initiation. Disubstituted olefin **11** does not react with **2e** even at elevated temperature. We conclude that internal olefins do not readily react with Mo benzylidynes.

We attempted to elucidate the mechanism of RCM of **3** catalyzed by **2e**. Monitoring the reaction of **3** in the presence of 5 mol % **2e** in C_6D_6 by ^1H NMR spectroscopy did not reveal any active intermediates. The catalyst remained intact according to the ^1H NMR spectra, while was **3** cleanly converted to **4** and ethylene. A possible explanation is that the dissociation of DME[32,36] is the rate-limiting step, and the following steps are too fast to be analyzed by the NMR method. All attempts to prepare DME-free **2e** failed. Heating **2e** in high vacuum at 100 °C led to slow decomposition of the complex. Reaction with $ZnCl_2$ in benzene at 80 °C and several cycles of dissolution/evaporation[28] of **2e** in toluene at 30 °C did not show any significant loss of DME.

During this work, we noticed that the reaction of p-$NO_2C_6H_4{-}C{\equiv}C{-}TMS$ with **1** produced **2d** as the major product (Scheme 2) along with a minor product that was insoluble in toluene and benzene but had limited solubility in dichloromethane and chloroform. That minor product was the DME-free complex $[p\text{-}NO_2C_6H_4C{\equiv}Mo(OC(CF_3)_2CH_3)_3]$ (**2f**). Somewhat surprisingly, the reaction of **3** with 2 mol % **2f** was complete in a few minutes at 22 °C. This supports the assumption that the dissociation of DME is the rate-limiting step for the reaction of **2e** with **3**.

We attempted to elucidate possible intermediates in the reaction of **3** with **2f**. Since **2f** is a highly active catalyst, the reaction was monitored by ^1H NMR spectroscopy at variable temperature starting from −40 °C. The resulting NMR spectra are quite complex (Figure 2; the full ^1H and ^{19}F NMR spectra are given in the Supporting Information). A few sets of signals assigned to intermediates (indicated by * in Figure 2) were observed, with the most pronounced changes at −10 °C, when the reaction starts to accelerate. The assignment of new signals to specific structures was not possible because of the low concentrations and overlap with signals of the substrate and products. It is worth mentioning that complex **2f** partially precipitates out from the reaction mixture at low temperature, so the concentration of the catalyst varied slightly during the experiment. However, the most significant result of this experiment is the fact that after reaction completion, the catalyst reformed its initial structure: when the reaction at 10 °C was 99% complete, all signals of the intermediates disappeared, and only the catalyst **2f** remained.

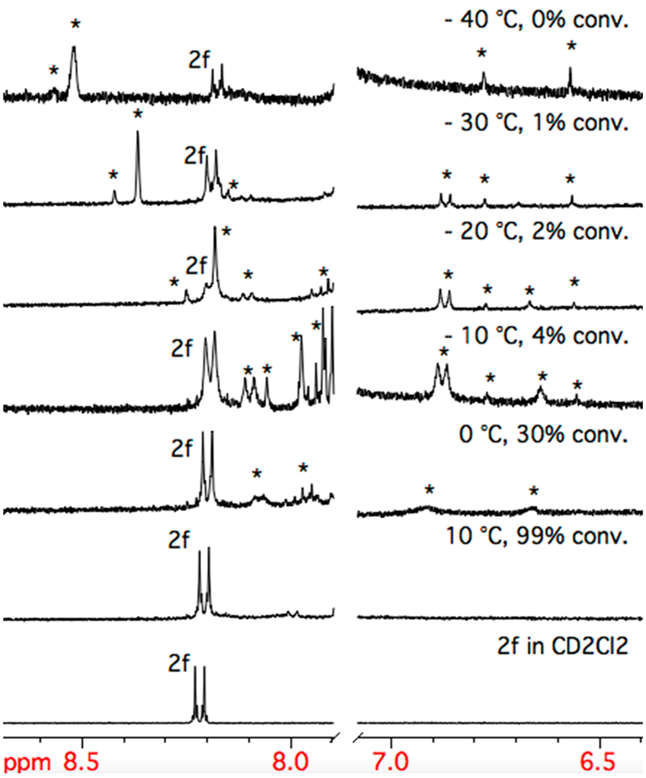
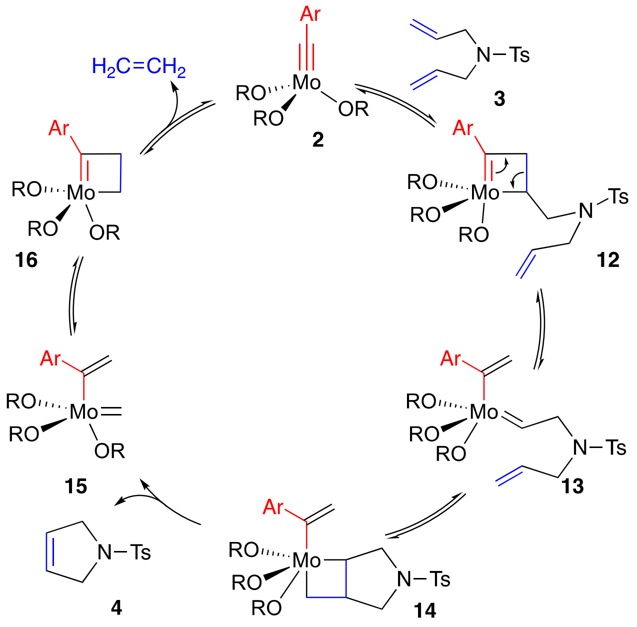


Figure 2. Aromatic region of the ^1H NMR spectra for the RCM reaction of **3** with ~1.5 mol % **2f** at variable temperature. The temperature and conversion toward **4** are indicated. Signals of intermediates are indicated by *. Bottom: NMR signal of two H atoms ortho to the nitro group in **2f**.

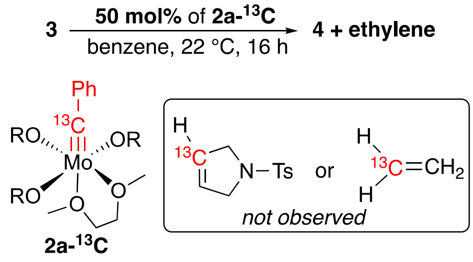
Scheme 4 illustrates the proposed mechanism. The key step is a [2 + 2] ynene cycloaddition with the formation of metallacyclobutene **12**. The ensuing cycloelimination gives alkylidene **13**, which is an active olefin metathesis catalyst. Metallacyclobutane **14** produces **4** and methylidene **15**. In the last step, metallacycle **16** makes ethylene and regenerates complex **2**. The reaction of **2f** with ethylene was attempted at variable temperature, but the formation of **16** was not been observed by ^1H NMR spectroscopy.

To support the proposed mechanism, we prepared ^{13}C-labeled benzylidyne **2a**-^{13}**C** and tested its reactivity toward **3** (Scheme 5). We did not observe the formation of ^{13}C-labeled

Scheme 4. Proposed Mechanism Based on a [2 + 2] Ynene Cycloaddition Reaction



Scheme 5. Reaction of 3 with ^{13}C-Labeled 2a



4 or ethylene by ^{13}C NMR spectroscopy, even at higher catalyst loadings. Thus, the intensity of olefinic carbon atoms in both products is the same as in the reaction with unlabeled **2a** (see the Supporting Information for details). Additionally, the ^{13}C benzylidyne peak stayed intact after the reaction. No other peaks in the region characteristic for Mo carbene or carbyne carbon resonance (200−400 ppm) were observed by ^{13}C NMR spectroscopy.

■ CONCLUSIONS

We have shown that Mo benzylidyne complexes can catalyze ring-closing metathesis, cross-metathesis, and ring-opening metathesis polymerization of alkenes. The active catalyst is a four-coordinate Mo complex containing benzylidyne and three hexafluoro-*tert*-butoxide ligands. The catalytic activity toward olefins depends on the electron-withdrawing groups on the benzylidyne and the nature of the olefin. The proposed mechanism includes the formation of a metallacyclobutene through [2 + 2] ynene cycloaddition and regeneration of the Mo benzylidyne after each catalytic cycle, as supported by ^{1}H and ^{13}C NMR studies. The latter distinguishes olefin metathesis catalyzed by metal carbyne complexes from traditional olefin, alkyne, and enyne metathesis transformations, where carbene or carbyne ligands in the initial complex change after the first catalytic cycle. Usually the nature of the carbene or carbyne ligands is more critical for the synthesis and isolation of the catalyst rather than for the catalysis itself, except for polymerization, where initiation should be faster than propagation to achieve a low polydispersity index. Olefin metathesis catalyzed by metal carbyne complexes provides an opportunity to affect the catalysis through the carbyne ligands, providing an additional tool to achieve desired properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00491.

Detailed experimental procedures, NMR data and spectra for all compounds, catalytic experiments, X-ray data for **2e**, and VT NMR spectra (PDF)

Cartesian coordinates for the structure **2e** (XYZ)

Accession Codes

CCDC 2018870 contains 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, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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