

Synthesis of Monoalkoxide Monopyrrolyl Complexes Mo(NR)(CHR')(OR'')(pyrrolyl): Enyne Metathesis with High Oxidation State Catalysts

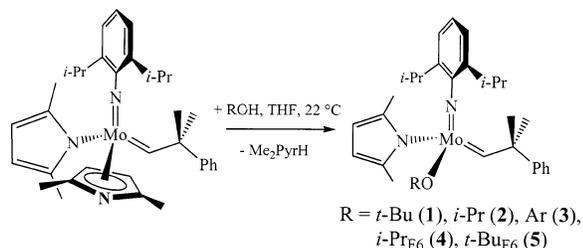
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We recently reported the synthesis, characterization, and reactivities of molybdenum bispyrrolyl complexes of the type Mo(NR)(CHR')(pyrrolyl)₂ where pyrrolyl is either the parent pyrrolyl¹ or 2,5-dimethylpyrrolyl (Me₂Pyr).² We are interested primarily in the use of bispyrrolyl species as precursors to bisalkoxide catalysts³ of the type Mo(NR)(CHR')(OR)₂ or Mo(NR)(CHR')(diolate) through addition of an alcohol or a diol to Mo(NR)(CHR')(pyrrolyl)₂ complexes. Preliminary experiments suggest that bispyrrolyls are less reactive toward olefins than bisalkoxide species, but serve as effective precursors to Mo-based bisalkoxides or diolates.^{1,2} We were attracted to the possibility that *monoalkoxide monopyrrolyl* species might be intercepted and might prove to be of interest in their own right. This expectation partly arises from the high reactivities observed for supported catalysts prepared through addition of bispyrrolyl species to silica⁴ where the predominant surface species is Mo(NR)(CHR')(pyrrolyl)(OSi_{surf}). High catalytic activities have been observed (and also rationalized through theoretical studies⁵) for these and related pseudotetrahedral metal complexes that are asymmetric at the metal center. We report here the synthesis of species of the type Mo(NR)(CHR')(OR'')(pyrrolyl) and their use in catalytic enyne metathesis reactions.⁶

Addition of 1 equiv of ROH to Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)₂ (Ar = 2,6-*i*-Pr₂C₆H₃; Me₂Pyr = 2,5-Me₂NC₄H₂) in diethyl ether or THF yields Mo(NAr)(CHCMe₂Ph)(OR)(Me₂Pyr) species where R = (CH₃)₃C (**1**, 22% isolated yield), (CH₃)₂CH (**2**, 83%), Ar (**3**, 81%), (CF₃)₂CH (**4**, 45%), or (CF₃)₂(CH₃)C (**5**, 80%) (eq 1). In



certain cases, Mo(NAr)(CHCMe₂Ph)(OR)₂ species are also formed, from which the Mo(NAr)(CHCMe₂Ph)(OR)(Me₂Pyr) species can be separated by selective crystallization. The *syn* alkylidene resonances are found in the proton NMR spectrum (C₆D₆) at 12.24 (**1**), 12.04 (**2**), 12.29 (**3**), 12.34 ppm (**4**), and 12.45 ppm (**5**) with *J*_{CH} ≈ 120 Hz in each case; no alkylidene resonances for *anti* isomers were observed. Results are likely to vary with the nature of the imido ligand. Preliminary studies have shown that an adamantylimido analogue of **3** cannot be prepared in a similar manner from a bispyrrolyl precursor; only the bisphenoxide species is formed.

An X-ray structure of **3** (Figure 1) showed that the alkylidene has the expected *syn* orientation, but although an η⁵-2,5-dimethylpyrrolyl ligand is possible electronically, an η¹-2,5-dimethylpyrrolyl is observed, presumably for steric reasons. It is not known whether

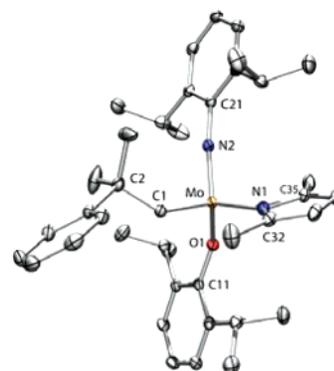


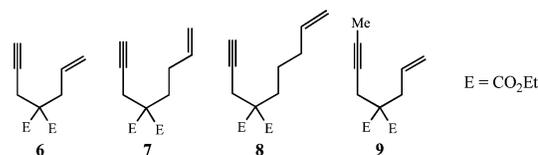
Figure 1. POV-ray drawing of **3**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Mo–N(2) = 1.7364(11) Å, Mo–C(1) = 1.8921(13) Å, Mo–O(1) = 1.9145(10) Å, Mo–N(1) = 2.0373(11) Å, Mo–N(2)–C(21) = 172.57(9)°, Mo–O–C(11) = 143.58(8)°, Mo–C(1)–C(2) = 139.48(9)°, Mo–N(1)–C(32) = 135.28(9)°.

complexes that contain smaller alkoxides contain an η¹- or an η⁵-pyrrolyl ligand. It also should be noted that η¹- and η⁵-pyrrolyl ligands interconvert readily at room temperature in Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)₂ species, and presumably also in Mo(NAr)(CHCMe₂Ph)(OR)(Me₂Pyr) species.

Ring-closing of diallyl ether catalyzed by compounds **1–5** (2 mol %) in C₆D₆ was complete within 15–20 min. In a separate experiment **3** was treated with 10 equiv of diallylether in C₆D₆ at room temperature a total of 10 times in sequence. Complete conversion of the substrate into products was observed in <10 min at each stage according to ¹H NMR spectroscopy. These observations suggest that monopyrrolyl monoalkoxide catalysts are relatively stable and long-lived, as observed in the metathesis of propylene by silica-supported catalysts of the same type in a flow reactor.⁴

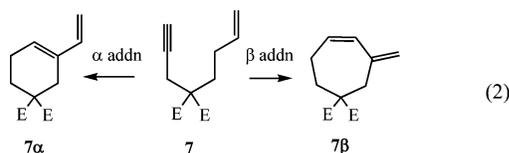
Mo-based monoalkoxides **1–5** were examined as possible enyne metathesis catalysts; enynes **6–9** served as substrates in these studies. Ring-closing enyne metathesis products are proposed to arise through initial addition of the triple bond to an intermediate methylene complex to give an α- or a β-substituted metallacyclobutene, followed by ring formation and reformation of the methylene species in the usual manner.⁶ For example, as illustrated in eq 2, enyne **7** could furnish **7α** or **7β** as a consequence of initial α or β addition, respectively. In the case of enyne **9**, product **9α** refers to the consequence of addition with the largest substituent in the α position of the initial metallacyclobutene. The results of these studies are summarized in Table 1.

Substrate **6** was converted exclusively into **6β**, the six-membered ring analogue of **7β**, in good isolated yield within 15 min using **4**

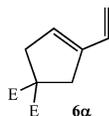


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or **5** (entries 4 and 5). However, **1**, **2**, or **3** did not afford any ring-closed product under similar reaction conditions, even though the initial alkylidenes disappeared immediately. Ru-carbene catalysts have been reported to afford **6α** in this reaction.^{6,7}



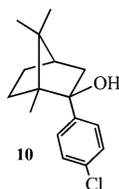
Treating **7** with 5 mol % of **3** or **5** in benzene-*d*₆ produced **7β** exclusively (entries 8 and 10). In contrast, **7α** and **7β** were both observed when **1**, **2**, or **4** was employed. Ru-carbene complexes afford **7α** in this reaction.^{6,7}

None of the expected ring-closed enyne metathesis products of substrate **8** was observed for **1–5** (entries 11–15). Compounds **1** and **2** led to formation of ethylene and what appears to be a dimer or oligomer mixture, the nature of which has not been elucidated.

In the case of substrate **9**, **4** and **5** yield mixtures of the two possible rings (entries 18 and 19). One might expect this result since the difference between the two types of initial metallacyclobutenes is not as marked compared to yields with substrates that contain a terminal triple bond. In contrast, **2** and **3** did not lead to any ring-closed product despite consumption of the initial alkylidene (entries 16 and 17).

The enyne metathesis results observed here cannot be explained solely on the basis of the relative sizes of the alkoxide in **1–5**, or upon their electronic properties. It also should be noted that only *syn* alkylidene isomers have been observed so far; nothing is known about *anti* isomers of Mo(NAr)(CHCMe₂Ph)(OR)(Me₂Pyr) and related species, the relative reactivity of *syn* and *anti* isomers, and the rate of interconversion of *syn* and *anti* isomers, all important issues for imido alkylidene catalysts of Mo and W that are generally difficult to address experimentally.^{3d} Finally, the role of the hapticity of the pyrrolyl in enyne metathesis is not known.

A potentially important property of the monoalkoxide compounds reported here is chirality at the metal center.⁸ Therefore, an enantiomerically pure alcohol should generate a mixture of diastereomers that may or may not interconvert rapidly. Upon addition of **10** to Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)₂, Mo(NAr)(CHCMe₂Ph)-



(OR*)(Me₂Pyr) (**11**) is isolated in 43% yield (where OR* is the alkoxide derived from **10**) as a mixture of two diastereomers with alkylidene proton resonances at 10.67 ppm (75%) and 11.79 ppm (25%). Recrystallization leads to a different ratio of diastereomers, thus confirming that diastereomers of **11** do not interconvert readily. The consequences for asymmetric metathesis reactions remain to be established and are the subject of ongoing investigations in these laboratories.

To the best of our knowledge, the reactions reported here are the first enyne metathesis reactions to be promoted by high

Table 1. Enyne Metathesis of Substrates **6**, **7**, **8**, and **9**^a

entry	cat (time)	subst	conv/products (%) ^b		yield (%)
			α	β	
1	1 (1.5 h)	6		<5 ^c	
2	2 (1.5 h)	6		<5 ^c	
3	3 (12 h)	6		<5 ^c	
4	4 (15 m)	6	0	100	68
5	5 (20 m)	6	0	100	72
6	1 (20 m)	7	60	40	77 ^{d,e}
7	2 (20 m)	7	80	20	79 ^{d,e}
8	3 (2 h)	7	0	100	70
9	4 (20 m)	7	30	70	83 ^{d,e}
10	5 (20 m)	7	0	100	70
11	1 (20 m)	8		40 ^f	
12	2 (12 h)	8		50 ^f	
13	3 (12 h)	8		<5 ^c	
14	4 (20 m)	8		<5 ^c	
15	5 (12 h)	8		<5 ^c	
16	2 (1.5 h)	9		<5 ^c	
17	3 (2 h)	9		<5 ^c	
18	4 (20 m)	9	40	60	72 ^d
19	5 (20 m)	9	25	75	80 ^d

^a All reactions were performed in C₆D₆ at 22 °C with 5 mol % catalyst loading and followed by ¹H NMR spectroscopy. ^b Based on disappearance of substrate. ^c The original alkylidene was consumed. ^d Isolated as a mixture of the two products. ^e Some homocoupling of the α product was observed. ^f The initial alkylidene was consumed and ethylene evolved; the products could not be identified.

oxidation state Mo catalysts. In certain cases, the products that are observed are different from those obtained through the use of Ru-based carbenes.⁹ It is important to note that all bisalkoxide or diolate catalysts that we have tried do *not* lead to controlled enyne metathesis, but to mixtures of ill-defined, possibly oligomeric, products. The modular nature of high oxidation state Mo or W complexes and the sensitivity of M(NR)(CHR')(X)(Y) complexes to variations in R, R', X, and Y continue to open avenues to the design and development of new catalysts. These investigations are also in progress and will be the subject of future reports.

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Supporting Information Available: Experimental details for the synthesis of all compounds and X-ray studies in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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