

Isolation of Pure Disubstituted *E* Olefins through Mo-Catalyzed *Z*-Selective Ethenolysis of Stereoisomeric Mixtures

Smaranda C. Marinescu,[†] Daniel S. Levine,[†] Yu Zhao,[†] Richard R. Schrock,^{*,†} and Amir H. Hoveyda[‡]

[†]Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

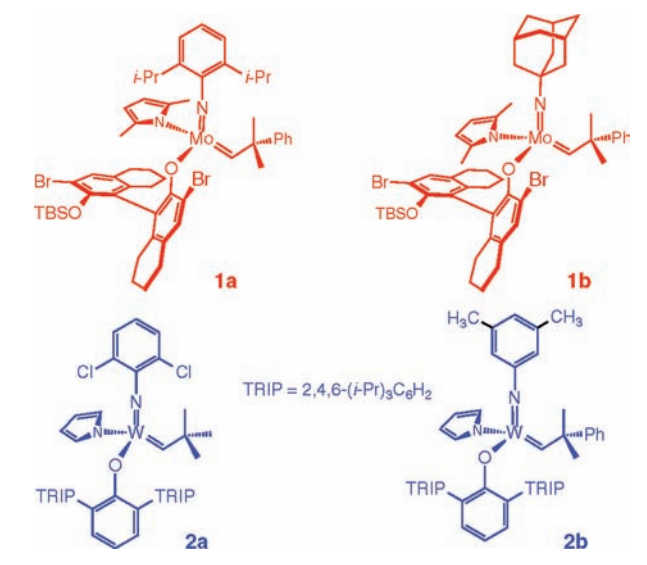
[‡]Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

S Supporting Information

ABSTRACT: Monoaryloxide–pyrrolide (MAP) complexes of molybdenum were employed for the selective ethenolysis of 1,2-disubstituted *Z* olefins in the presence of the corresponding *E* olefins. Reactions were performed in the presence of 0.02–3.0 mol % catalyst at 22 °C under 20 atm ethylene. We have demonstrated that the *Z* isomer of an easily accessible *E*:*Z* mixture can be destroyed through ethenolysis and the *E* alkene thereby isolated readily in high yield and exceptional stereoisomeric purity.

During the last four years, research in these laboratories has led to the discovery and development of monoaryloxide–pyrrolide (MAP) complexes **1** and **2** (among others; Scheme 1).

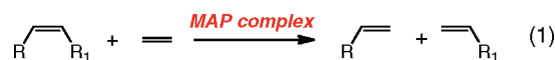
Scheme 1. Representative Mo- and W-Based MAP Complexes



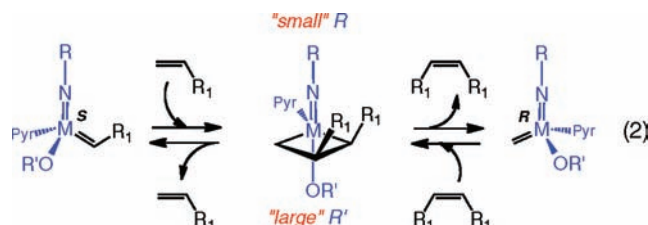
Variations have proven to be especially efficient catalysts for enantioselective ring-closing,¹ enantioselective and *Z*-selective ring-opening/cross-metathesis,² and *Z*-selective homocoupling³ and cross-metathesis reactions.⁴ We have attributed the origin of the *Z* selectivity to the presence of a relatively large monoaryloxide, often in combination with a relatively small imido group. An important feature of MAP catalysts is that they contain a stereogenic metal center. Since the aryloxide in

1 is enantiomerically pure, two diastereomers are formed, one of which is more reactive and leads to high enantioselectivity.⁵ Ring-opening metathesis polymerization reactions promoted by Mo complexes analogous to **2** give >95% *cis* syndiotactic polymers, with the syndiotacticity being a consequence of directed addition of the monomer *trans* to the pyrrolide and inversion of configuration at the metal center with each insertion of monomer.⁶

Many MAP catalysts are unusually efficient, perhaps in part as a consequence of the fact that highly reactive methylidene species are relatively stable.⁷ Long-lived reactive methylidene species and the lability of unsubstituted molybdacyclobutane intermediates toward loss of ethylene allow the efficient ethenolysis of methyl oleate [eq 1; R = (CH₂)₇CH₃, R₁ = (CH₂)₇CO₂CH₃] with 0.02 mol % **1a** at room temperature and 10 atm ethylene to give 1-decene and methyl-9-decenoate selectively (>99%) and essentially completely (95%).⁸



Ethenolysis involving ethylene and (*Z*)-R₁CH=CHR₁ is the reverse of *Z*-selective metathesis coupling of R₁CH=CH₂; that is, the same α,β -disubstituted metallacyclobutane complex must be formed as an intermediate in the forward reaction (homometathesis coupling; see eq 2) as in the reverse reaction (ethenolysis). Therefore, ethenolysis could be significantly more facile for the *Z* isomer than the *E* isomer under the right circumstances. It should be noted that the olefins involved in the forward and reverse reactions shown in eq 2 are coordinated *trans* to the pyrrolide ligand and that the configuration at the metal is inverted in each metathesis step.^{1b,7,9}

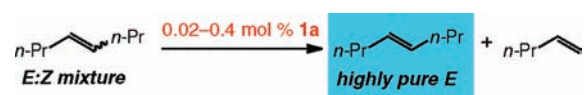


To explore the proposal that *Z* olefins can be more prone to ethenolysis than *E* olefins, 0.4 mol % **1a** was added to a 1:4 mixture (thermodynamic) of (*Z*)-4-octene and (*E*)-4-octene

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Table 1. Mo-Catalyzed Z-Selective Ethenolysis of a 4:1 E:Z Mixture of 4-Octenes^a



entry 1	mol % 1a	pressure (atm)	time	yield of E ^b	final % E ^c
1	0.4	4	15 min	79	>98
2	0.1	4	1 h	76	91
3	0.1	20	1 h	77	97
4	0.2	20	1 h	71	89
5	0.05	20	4 h	62	>98
6	0.02	20	18 h	77	>98




^a Performed under a N₂ atmosphere; see the SI for full details. ^b Percent yield of pure E isomers after purification (±5%); theoretical value = 80%. ^c Determined through analysis of 400 MHz ¹H NMR spectra (±2%).

(0.6 M in C₆D₆), and the evacuated vessel was pressurized with ethylene (4 atm). After 15 min, the solution was exposed to air, filtered through alumina, and analyzed by ¹H and ¹³C NMR spectroscopy and gas chromatography. The product mixture contained 1-pentene and >98% (E)-4-octene (79% yield; Table 1, entry 1). The results of ethenolysis of neat 4:1 E:Z mixtures of 4-octenes, illustrated in entries 2–6 of Table 1, suggest that low catalyst loadings, 20 atm pressure, and neat substrate produce the best results. The most efficient process corresponds to ethenolysis with 0.02 mol % 1a under 20 atm ethylene (entry 6). The product is readily recovered by passing the mixture through a plug of silica gel and removing the light olefin in vacuo.

Next, we set out to compare the rates of ethenolysis of (Z)-4-octene and (E)-4-octene carried out in the presence of 1a. We assumed that the rate would be first-order in catalyst, ethylene, and substrate. Reactions were performed without solvent under 20 atm ethylene; catalyst loadings for the reaction of (E)-4-octene were 20 or 25 times higher than those employed for (Z)-4-octene. The points in the plots of ln(C/C₀) versus time consisted of individual runs [seven runs for (E)-4-octene and 11 runs for (Z)-4-octene; see the Supporting Information (SI)]. Comparison of the plot for (E)-4-octene (R² = 0.98) with that for (Z)-4-octene (R² = 0.86) allowed us to deduce a value of 30 ± 5 for the quantity R_{Z/E} = k_Z/k_E, where k_Z and k_E are the rate constants for ethenolysis of the Z and E olefins. The large error arises from uncertainties in both k_Z and k_E (see the SI). For example, between 3.2 and 9.3% (Z)-4-octene was present upon workup in runs involving (E)-4-octene. Two possible explanations for the formation of (Z)-4-octene are Z-selective metathesis homocoupling of 1-pentene upon release of the ethylene pressure before deactivation of the catalyst (a homocoupling “back-reaction”) or direct isomerization of E to Z via a trisubstituted metallacyclobutane. At this stage it is not known whether catalyst decomposition in a long run with the lowest catalyst loading (entry 6) limited the consumption of (E)-4-octene and preserved the final % E level.

A value of 30 for R_{Z/E} [calculated as ln([Z]/[Z]₀)/ln([E]/[E]₀)] is sufficient to produce most of the findings shown in Table 1, but this method of determining R_{Z/E} is prone to large errors. A direct measure of the relative rates of consumption of two substrates with compensation for the catalyst concentration using the approximate suspected value of R_{Z/E} appears to be a more reliable method of measuring R_{Z/E} at this stage.

Table 2. Mo-Catalyzed Z-Selective Ethenolysis of E:Z Olefin Mixtures^a

entry	substrate	Initial E:Z	mol % 1a	pressure (atm)	time	yield of E ^b	final % E ^c
1	Me-  -n-pent	1:4	0.02	20	18 h	20	>98
2	Et-  -OEt	1.1:1	2.0	4	2 h	48	>98
3	n-Bu-  -OCOMe	5:1	1.0	4	15 min	75	>98
4	(Z)-4-octene & (E)-5-decene	1:1	2.0	4	15 min	45	96

^{a–c} See Table 1.

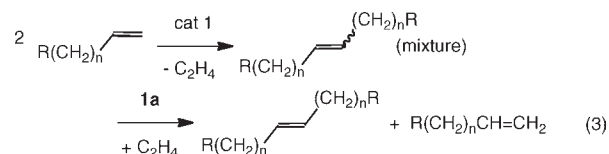
Table 3. Two-Step Synthesis of (E)-R(CH₂)_nCH=CH-(CH₂)_nR^a

entry	R; n	initial E:Z	mol % 1a	pressure (atm)	time	yield of E ^b	final % E ^c
1	Me; 5	4:1	0.5	20	4 h	67	>98
2	Me; 7	4:1	2.0	4	15 min	77	>98
3	Cy; 1	4:1	3.0	4	15 min	78	>98
4	Ph; 1	4:1	0.5	20	5 h	67	>98
5	CO ₂ Me; 8	3:1	0.5	20	20 h	56	>98
6	CO ₂ Et; 7	2.4:1	0.5	20	4 h	66	>98
7	OBn; 1	11:1	1.0	4	30 min	85	>98

^{a–c} See Table 1. The E:Z mixture was prepared with MoF12 in runs 1–3 and 7 and 1a in runs 4–6.

Other examples of the generation of pure E olefins through ethenolysis of a mixture of stereoisomers are shown in Table 2. For example, ethenolysis of a neat 1:4 E:Z mixture of 2-octenes with 0.02 mol % 1a and ethylene (20 atm) led to the formation >98% (E)-2-octene (20%) after removal of terminal olefins formed through reaction of the Z isomer (Table 2, entry 1). It is likely that the efficiency of the ethenolysis of functionalized olefins illustrated in entries 2 and 3 is limited by reaction of the catalyst with low levels of debilitating impurities (e.g., alcohol, aldehyde, acid). In run 4, essentially no C₉ olefin was formed, which suggests that there is no significant homocoupling back-reaction between 1-hexene and 1-pentene under these conditions.

The data presented in Tables 1 and 2 indicate that it should be possible to access stereoisomerically pure symmetric E olefins from terminal olefins by a two-step process. First, Mo(NAr)(CHCMe₂Ph)[OC(CF₃)₂Me]₂ (MoF12; Ar = 2,6-i-Pr₂C₆H₃) or 1a (cat 1; eq 3) was employed to homocouple R(CH₂)_nCH=CH₂ to give an E:Z mixture. This product mixture was then passed through a short silica plug to remove any active Mo catalyst. The eluant was then subjected to Z-selective ethenolysis employing 1a, leaving (E)-R(CH₂)_nCH=CH(CH₂)_nR in >98% stereoisomeric purity and high yield (relative to theory) in all cases (Table 3).



We were surprised initially to find that a catalyst that is stable toward ethylene and contains the ligand O-2,6-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃ (OHIPT) is inferior for Z-selective ethenolysis. For example, only ~1% (Z)-4-octene (0.2 M in C₆D₆) was

consumed in 45 min under 20 atm of ethylene when 1 mol % Mo(NAr)(CHCMe₂Ph)(Pyr)(OHIPT)³ (Pyr = NC₄H₄⁻) was employed. The reason for such a low level of activity might be that the unsubstituted molybdacyclobutane does not readily lose ethylene. Detailed NMR studies have shown that a Mo(CH₂CH₂CH₂) species is converted to a Mo(CH₂)(CH₂CH₂) intermediate with $k_f = 14\,500\text{ s}^{-1}$ and $k_r = 4900\text{ s}^{-1}$ in the case of the metallacyclobutane Mo(NAr)(C₃H₆)(OBr₂Bitet)(Me₂Pyr), where OBr₂Bitet is the biphenolate in **1a** and Me₂Pyr = NC₄Me₂H₂⁻.⁷ In contrast, for the same transformation in Mo(NAr)(C₃H₆)(OHIPT)(Pyr), k_f and k_r were found to be 1.8 and 9.0 s⁻¹, respectively (20 °C, toluene-*d*₈ in both cases). Differences in the k_f values (by a factor of ~8000) and the equilibrium constants (3.0 and 0.2, respectively) could account for the inability of the OHIPT-bearing catalysts tried to date to promote Z-selective ethenolysis efficiently.

The relatively high stability of tungstacyclobutane complexes toward release of ethylene also limits the effectiveness of tungsten-based catalysts for ethenolysis. It has been found that the intermediate W(CH₂)(CH₂CH₂) complex is formed from W(NAr)(C₃H₆)(OBr₂Bitet)(Me₂Pyr) with $k_f = 3.2\text{ s}^{-1}$ and $k_r = 69\text{ s}^{-1}$.³ Therefore, to date, Mo-OBr₂Bitet catalysts appear to be optimal for ethenolysis. The reason why unsubstituted metallacyclobutanes of OHIPT species are so much more stable toward loss of ethylene than OBr₂Bitet species might be a consequence of the substantially larger size of an OHIPT ligand relative to a OBr₂Bitet ligand. Subtle steric factors also may prove to be critical if the ethylene axis is required to be approximately perpendicular to the M=CH₂ axis in the M(CH₂)(CH₂CH₂) intermediate in order for ethylene to be lost readily.¹⁰

It should be noted that only catalyst **1a** has been successful in reported Z-selective ethenolysis to date, that **1a** is a mixture of diastereomers that interconvert readily in the presence of ethylene,¹ and that **1a** is not an especially successful Z-selective homocoupling catalyst.^{3a,b} A detailed mechanistic understanding of Z-selective ethenolysis that includes a discussion of the interconversion and relative rates of reaction of diastereomers of any possible intermediate alkylidene may be necessary to explain all of the experimental observations eventually, but such an understanding is not at present within reach. It remains to be seen which catalysts, if any, that do *not* form diastereomers are successful for Z-selective ethenolysis.

Molybdenum-catalyzed Z-selective ethenolysis should allow access to a large variety of E olefins that otherwise would be more difficult to prepare in high stereoisomeric purity through alternative methods. This indirect synthesis of E olefins complements the direct synthesis of Z olefins through Z-selective metathesis reported in earlier papers. The design and development of more efficient catalyst systems and exploration of the scope of Z-selective ethenolysis are in progress.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectral and analytical data for all reaction products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

rrs@mit.edu

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