

Supporting Information for

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

by

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**General.** All manipulations of air- and moisture-sensitive materials were conducted under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a dual-manifold Schlenk line. The glassware, including NMR tubes were oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns and stored over 4 Å Linde-type molecular sieves. Dimethoxyethane, *cis*-4-octene, *trans*-4-octene, 2-octene, and 1-octene were vacuum distilled from a dark purple solution of sodium benzophenone ketyl, and degassed three times by freeze-pump-thaw technique. 1-Decene, allylcyclohexane, allylbenzene, methyl-10-undecenoate, ethyl-9-decenoate, and allyl benzyl ether were dried over CaH<sub>2</sub>. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. Proton and carbon NMR spectra were acquired at room temperature unless otherwise noted through the use of Varian spectrometers and referenced to the residual <sup>1</sup>H/<sup>13</sup>C resonances of the deuterated solvent (<sup>1</sup>H: CDCl<sub>3</sub>, δ 7.26; C<sub>6</sub>D<sub>6</sub>, δ 7.16; CD<sub>2</sub>Cl<sub>2</sub>, δ 5.32; C<sub>7</sub>D<sub>8</sub>, δ 7.09, 7.00, 6.98, 2.09. <sup>13</sup>C: CDCl<sub>3</sub>, δ 77.23; C<sub>6</sub>D<sub>6</sub>, δ 128.39; CD<sub>2</sub>Cl<sub>2</sub>, δ 54.00; C<sub>7</sub>D<sub>8</sub>, δ 137.86, 129.24, 128.33, 125.49, 20.4) and are reported as parts per million relative to tetramethylsilane. The high-pressure vessel equipped with a pressure gauge was purchased from Parr Instrument Company, Moline, Illinois.

**General Ethenolysis Procedure at 4 atm.** Ethenolysis reactions were set up under an inert atmosphere in a glovebox. A 25 mL Schlenk round bottom flask equipped with a magnetic stir bar and a side arm was charged with a C<sub>6</sub>D<sub>6</sub> solution (1.0 mL) of the catalyst and the desired olefin. The reaction mixture was connected to a Schlenk line, degassed (three times) and 100 mL of ethylene were condensed into the flask at liquid nitrogen temperature. The flask was closed and allowed to warm up to room temperature; the reaction mixture was stirred with a magnetic stir bar. Approximately 5.6 mL of ethylene are consumed so the pressure at the end of the reaction is ~3.8 atm. The reaction was quenched by exposure to air. The E:Z ratio of the unreacted starting material was analyzed by <sup>1</sup>H and <sup>13</sup>C NMR (CDCl<sub>3</sub> as the solvent) on a Varian 500 MHz spectrometer. The crude reaction mixture was then purified by silica gel chromatography or distillation and the recovered starting material (*E*-olefins) was isolated in a pure form with the isolated yield indicated in the text.

**General Ethenolysis Procedure at 20 atm.** Ethenolysis reactions were set up under an inert atmosphere in a glovebox. A high pressure vessel equipped with a vial (24 x 62 mm) containing a magnetic stir bar (3 x 10 mm) was charged with a stock solution of the catalyst and the appropriate amount of olefin (or mixture of olefins). The vessel was sealed and taken out of the glovebox and connected to a Schlenk line. The vessel was then pressurized to 20 atm of ethylene

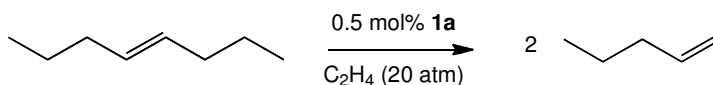
and the reaction mixture was stirred at room temperature. After the specified time the reaction was quenched by exposure to air. The E:Z ratio of the unreacted starting material was analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  as the solvent) on a Varian 500 MHz spectrometer. The crude reaction mixture was then purified by silica gel chromatography and the recovered starting material (*E*-olefins) was isolated in a pure form with the isolated yield indicated in the text.

**Kinetic studies.** In the ethenolysis of *E*-4-octene the final product contained *Z*-4-octene (Table 1). We propose that the *Z*-4-octene arises through a back reaction when the 20 atm pressure is released and before the catalyst is deactivated through exposure to air. Therefore, the % *Z*-4-octene is added to the % *E*-4-octene that has been converted in order to obtain the amount of *E*-4-octene that has actually been consumed through ethenolysis. As a consequence of the comparatively low catalyst loadings in the ethenolysis of *Z*-4-octene, we assumed that the back reaction to reform *Z*-4-octene upon release of pressure would be negligible.

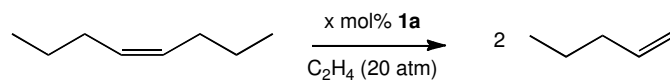
If we assume that  $\ln([Z]/[Z]_0) = -k_Z[\text{C}_2\text{H}_4][\text{cat}]t$  and  $\ln([E]/[E]_0) = -k_E[\text{C}_2\text{H}_4][\text{cat}]t$ , then  $\ln([Z]/[Z]_0)/\ln([E]/[E]_0) = k_Z/k_E = R_{Z/E}$ . In each case  $k_{\text{obs}} = k[\text{C}_2\text{H}_4][\text{cat}]$ , but  $[\text{C}_2\text{H}_4]$  and  $[\text{cat}]$  need not be known in order to obtain  $R_{Z/E}$ .

In Table 1 the conversion values can either include the %*Z* (if *Z* is assumed to arise through *Z*-selective homocoupling) or not (if it is assumed to arise through direct isomerization of *E* to *Z*.)

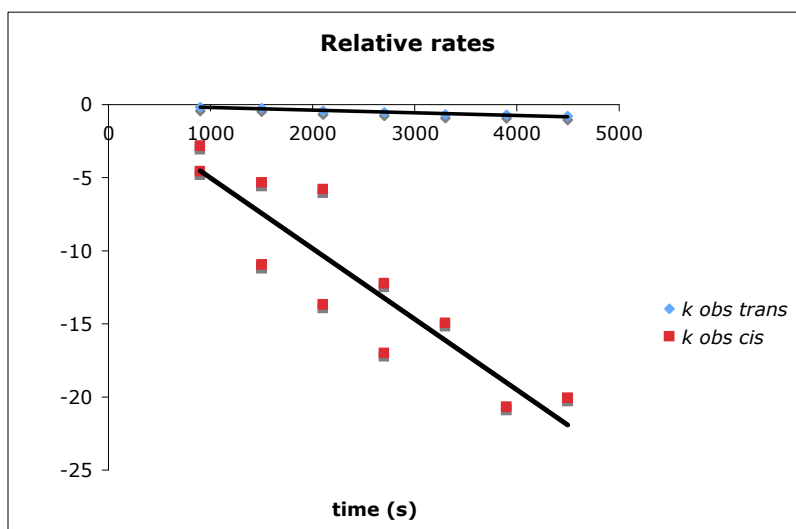
**Table 1.** Kinetic study of the ethenolysis of *E*-4-octene.



Entry	time (min)	Conv.	%Z	Corrected Conv.
1	15	13.7	3.3	17.0
2	25	18.6	3.2	21.8
3	35	26.7	7.8	34.5
4	45	34.1	7.1	41.2
5	55	39.1	9.3	48.4
6	65	43.3	7.3	50.6
7	75	49.0	6.3	55.3

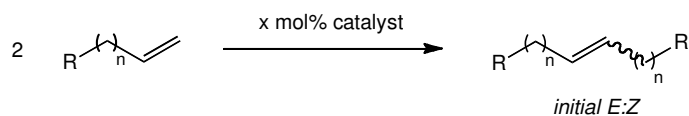
**Table 2.** Kinetic study of the ethenolysis of *Z*-4-octene.

Entry	x	time (min)	Conv.
1	0.025	15	20.5
2	0.025	25	42.2
3	0.025	35	49.5
4	0.025	45	57.2
5	0.025	55	52.6
6	0.025	65	64.4
7	0.025	75	63.3
8	0.02	15	10.7
9	0.02	25	19.3
10	0.02	35	20.7
11	0.02	45	38.7

**Figure 1.** Comparison of  $k_{\text{obs}}$  for the ethenolysis of *Z*-4-octene and *E*-4-octene, assuming that *Z*-4-octene arises during ethenolysis of *E*-4-octene through a homocoupling of 1-pentene.

**General Procedure for the Homocoupling of  $\alpha$ -Olefins.** A 1 dram vial equipped with a magnetic stir bar was charged with the stated amount of the catalyst and solvent (pentane or benzene). The desired olefin was added through a syringe. The reaction mixture was stirred at room temperature until the starting material was completely consumed. The reaction mixture was then exposed to air and passed through a short silica gel plug. The eluent was analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

**Table 3.** Homocoupling of  $\alpha$ -Olefins.



Entry	R	n	Catalyst	x	time	Initial E:Z
1	Me	5	Mo(NAr)(CHR)[OCMe <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	4	2 h	4
2	Me	7	Mo(NAr)(CHR)[OCMe <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	4	15 min	4
3	Cy	1	Mo(NAr)(CHR)[OCMe <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	4	15 min	4
4	Ph	1	<b>1a</b>	4	16 h	4
5	CO <sub>2</sub> Me	8	<b>1a</b>	2	16 h	3
6	CO <sub>2</sub> Et	7	<b>1a</b>	2	16 h	2.4
7	OBn	1	Mo(NAr)(CHR)[OCMe <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	4	16 h	11

R = CMe<sub>2</sub>Ph