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Ethenolysis Reactions Catalyzed by Imido Alkylidene Monoaryloxide Monopyrrolide (MAP) Complexes of Molybdenum

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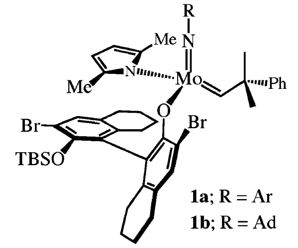
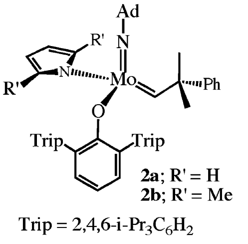
We have reported recently that monoaryloxide-pyrrolide (MAP) olefin metathesis catalysts **1** and **2**, which can be prepared through addition of a phenol to a bispyrrolide,[1] can be especially efficient for enantioselective and/or *Z*-selective reactions.[2−4] In the process of studying related tungsten MAP complexes[5] we noticed that some methylidene species could be unusually stable, yet highly reactive. For example, a 0.04 M solution of $W(NAr)(CH_2)(O\text{-}2,3,5,6\text{-}Ph_4C_6H)(Me_2Pyr)$ (Me_2Pyr = 2,5-dimethylpyrrolide) in toluene-d_8 could be heated to 80 °C without significant decomposition of the tungsten species after ∼1 h. The stability of methylidene species is likely to be an important feature of MAP species that are especially efficient in a reaction in which ethylene is present. Long-lived, reactive methylidene species and the lability of unsubstituted metallacyclobutane intermediates[5,6] suggest that efficient *ethenolysis* of internal linear (eq 1) or cyclic olefins may be possible. Efficient ethenolysis of a natural product such as methyl oleate is attractive as a method for obtaining useful chemicals from biomass.[7] We show here that ethenolysis reactions that employ molybdenum-based MAP species can be highly efficient at *room temperature* and readily accessible pressures of ethylene.



1a; R = Ar
1b; R = Ad



2a; R' = H
2b; R' = Me
Trip = 2,4,6-i-$Pr_3C_6H_2$

$$RCH{=}CHR' + CH_2{=}CH_2 \rightarrow RCH{=}CH_2 + R'CH{=}CH_2 \qquad (1)$$

Exposure of **1a** to 1 atm of ethylene has been shown to lead to mixtures that contain the two diastereomers of **1a**, the two diastereomers of $Mo(NAr)(CH_2)(Me_2Pyr)(OBitet)$, the unsubstituted molybdacyclobutane complex, $Mo(NAr)(CH_2CH_2CH_2)(Me_2Pyr)(OBitet)$, and $CH_2{=}CHCMe_2Ph$, along with ethylene (OBitet is the aryloxide in **1**).[6] A reaction between $Mo(NAr)(CHCMe_3)(Me_2Pyr)(OBitet)$ and ethylene allowed the molybdacyclobutane complex, $Mo(NAr)(CH_2CH_2CH_2)(Me_2Pyr)(OBitet)$, to be isolated at −30 °C in the presence of ethylene (1 atm). An X-ray structural study reveals it to have the TBP structure shown in Figure 1, one that is virtually identical to the structure found for $W(NAr)(CH_2CH_2CH_2)(Me_2Pyr)(OBitet)$.[5] Molybdacyclobutane species are especially rare because they lose an olefin readily.[8] To the best of our knowledge only one other molybdacyclobutane, a *square pyramidal* bis-*tert*-butoxide species, has been structurally characterized.[9] Metallacyclobutanes that have a TBP structure are proposed to lose an olefin more readily than an SP species.[8] When ethylene is removed above a solution of $Mo(NAr)(CH_2CH_2CH_2)(Me_2Pyr)(OBitet)$, mixtures of the two diastereomers of $Mo(NAr)(CH_2)(Me_2Pyr)(OBitet)$ (δH_α = 12.35 and 12.13 ppm, 12.94 and 12.24 ppm) are observed.[6] The two diastereomers of $Mo(NAr)(CH_2)(Me_2Pyr)(OBitet)$ decompose to a significant degree in the absence of ethylene over a period of 1−2 days.

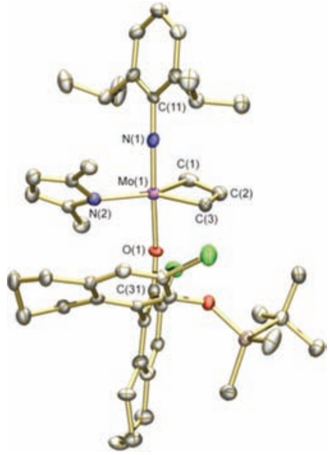


Figure 1. POV-ray drawing of $Mo(NAr)(C_3H_6)(Me_2Pyr)(OBitet)$. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo−C(1) = 2.056(7); Mo−C(3) = 2.052(5); Mo−C(2) = 2.332(6); C(1)−C(2) = 1.609(11); C(2)−C(3) = 1.568(10); Mo−C(1)−C(2) = 78.0(4); Mo−C(3)−C(2) = 79.0(4); C(1)−C(2)−C(3) = 119.2(5); C(1)−Mo−C(3) = 83.7(3).

Ethenolysis (employing 99.5% pure ethylene) of methyl oleate (Table 1) initiated by **1a** at room temperature yields essentially only 1-decene (1D) and methyl-9-decenoate (M9D) with a selectivity of >99% and yields up to 95% (entries 1−4). (The other possible products are 1,18-dimethyl-9-octadecenedioate and 9-octadecene.) The highest turnovers are found at the higher pressures (compare entry 3 vs 4). All results are consistent with time dependent catalyst decomposition and a (low) solubility of ethylene in methyl oleate that limits conversion at low pressures. The catalysts shown in entries 5−7 produce products with lower selectivities and yields. An OBitet catalyst that contains the adamantylimido ligand (**1b**, entry 8) is almost as successful as **1a**, but two catalysts closely related to **1a** and **1b** (entries 9 and 10) gave no product; the reasons are not yet known. A run employing 10 000 equiv of methyl oleate at 20 atm of ethylene led to only ∼10% conversion.

Tungstacyclobutane catalysts[5] (entries 11 and 12) produced results that were inferior to molybdenum catalysts in yield, either at room temperature or at 50 °C, although selectivity was still >99%. Since it is likely that the rate-limiting step in ethenolysis is loss of ethylene from an unsubstituted metallacyclobutane, one possible

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Table 1. Ethenolysis of Methyl Oleate (MO)

entry	catalyst	equiv	*P* (atm)	time (h)	% conv[a]	% select[b]	% yield[c]	TON[d]
1	Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(OBitet) (**1a**)	500	4	1	94	>99	94	470
2	**1a**	1000	4	20	80	>99	80	800
3	**1a**	5000	4	15 or 48	58	>99	58	2900
4	**1a**	5000	10	15	95	>99	95	4750
5	Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$	500	4	2	83	76	63	315
6	Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(TPP)	500	4	20	87	86	75	325
7	Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(OSiPh$_3$)	500	4	1	86	92	79	395
8	Mo(NAd)(CHCMe$_2$Ph)(Me$_2$pyr)(OBitet) (**1b**)	500	4	18	96	98	94	470
9	Mo(NAd)(CHCMe$_2$Ph)(Pyr)(HIPTO) (**2a**)	50	4	1	0	0	0	0
10	Mo(NAd)(CHCMe$_2$Ph)(Me$_2$pyr)(TPP)	50	4	1	0	0	0	0
11	W(NAr)(C$_3$H$_6$)(Me$_2$pyr)(OBitet)	500	4	17	48	>99	48	240
12	W(NAr)(C$_3$H$_6$)(Me$_2$pyr)(OBitet) (50 °C)	500	4	18	62	>99	62	310

[a] Conversion = 100 − [(final moles of MO) × 100/(initial moles of MO)]. [b] Selectivity = (1D + M9D) × 100/(total products). [c] Yield = (1D or M9D) × 100/(initial moles of MO). [d] TON = % yield[(moles of MO)/(moles of catalyst)].

reason why tungsten is slower than molybdenum is that tungstacyclobutanes release ethylene more slowly than molybdacyclobutanes.[5] Another possibility is that the ester carbonyl binds to tungsten more strongly than it does to molybdenum and inhibits turnover to a more significant degree.

Ethenolysis of 30 000 equiv of cyclooctene to give 1,9-decadiene with **1a** as the catalyst proceeded with a TON of 22 500 (75% yield) at 20 atm (Table 2). Initiation of polymerization of cyclooctene with **1a** is slow, so little **1a** is consumed before it reacts with ethylene to yield Mo(NAr)(CH$_2$)(Me$_2$Pyr)(OBitet), and ethenolysis then proceeds rapidly. At 1 atm of ethylene in an NMR scale reaction, poly(cyclooctene) can be observed, but the amount of polymer decreases substantially upon addition of more ethylene. Essentially the same result as shown in entry 5 of Table 2 was observed when commercial 99.995% ethylene was employed. Therefore any potentially harmful impurities in the 99.5% ethylene (e.g., water or oxygen) do not limit the TON.

Table 2. Ethenolysis of Cyclooctene with **1a**

entry	equiv	*P* (atm)	*T* (h)	% conv	% yld	TON
1	5000	10	16	98	90	4500
2	10 000	10	20	98	80	8000
3	10 000	20	20	93	93	9300
4	20 000	20	16	88	88	17 600
5	30 000	20	20	75	75	22 500

Ethenolysis of 5000 equiv of cyclopentene at 20 atm of 99.5% ethylene led to an 84% conversion to 1,6-heptadiene in 79% yield in 15 h (TON 3950). In a run employing 10 000 equiv of cyclopentene and 99.995% ethylene, the yield is 58% and TON 5800 in 20 h.

It currently is not known why Mo(NAr)(CH$_2$)(Me$_2$Pyr)(OBitet) methylene species are relatively long-lived. Although the main mode of methylidene decomposition is bimolecular coupling to give ethylene, some evidence in the literature suggests that ethylene promotes rearrangement of a metallacyclobutane to an olefin in certain circumstances.[10] If the latter mode of decomposition is operating in the ethenolysis reactions described here, further engineering of the catalyst may sterically prevent formation of a six-coordinate ethylene adduct that leads to metallacycle rearrangement.

The results in Table 1 suggest that a key to high selectivity is relatively slow productive metathesis to yield 1,18-dimethyl-9-octadecenedioate and 9-octadecene (for steric reasons), i.e., slow reaction between a *substituted* alkylidene and 1D, M9D, or methyl oleate (the slowest) under the conditions employed. We have no reason to expect that the turnover numbers have been maximized with **1a**. The *chirality* of the OBitet ligand seems unlikely to have much, if anything, to do with its efficiency as an ethenolysis catalyst, since catalysts such as those shown in entries 6 and 7 are relatively successful. The number of possible catalyst variations is large, so we expect that fine-tuning ultimately should lead to even more efficient catalysts for ethenolysis.

Ethenolysis of methyl oleate by ruthenium catalysts has been studied extensively.[7] Conversion to products at 10 atm of ethylene usually is incomplete and/or unselective to 1D and M9D, and no efficient reactions have been reported at room temperature. In the most successful case reported here, routinely purified methyl oleate can be converted virtually completely to 1D and M9D at room temperature and 10 atm of ethylene.

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Supporting Information Available: Experimental details for the synthesis of all compounds and the X-ray structural study. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Hock, A. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373. (b) Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654. (c) Marinescu, S. C.; Singh, R.; Hock, A. S.; Wampler, K. M.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 6570. (d) Schrock, R. R. *Chem. Rev.* **2009**, *109*, online 3/13. (e) Two Mo(NAr)(CHCMe$_2$Ph)(pyrrolide)$_2$ complexes are sold by Strem Chemicals, Inc.

(2) (a) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2008**, *456*, 933. (b) Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 943.

(3) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844.

(4) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962.

(5) Jiang, A. J.; Simpson, J. H.; Müller, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 7770.

(6) Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 58.

(7) (a) Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. *Organometallics* **2004**, *23*, 2027. (b) Schrodi, Y.; Ung, T.; Vargas, A.; Mkrtumyan, G.; Lee, C. W.; Champagne, T. M.; Pederson, R. L.; Hong, S. H. *Clean: Soil, Air, Water* **2008**, *36*, 669. (c) Bei, X.; Allen, D. P.; Pederson, R. L. *Pharm. Technol.* **2008**, s18. (d) Anderson, D. R.; Ung, T.; Mkrtumyan, G.; Bertrand, G.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2008**, *27*, 563. (e) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411. (f) Forman, G. S.; McConnell, A. E.; Hanton, M. J.; Slawin, A. M. Z.; Tooze, R. P.; vanRensburg, W. J.; Meyer, W. H.; Dwyer, C.; Kirk, M. M.; Serfontein, D. W. *Organometallics* **2004**, *23*, 4824.

(8) (a) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (b) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

(9) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.

(10) (a) Tsang, W. C. P.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2001**, *20*, 5658. (b) Leduc, A.-M.; Salameh, A.; Soulivong, D.; Chabanas, M.; Basset, J.-M.; Coperet, C.; Solans-Monfort, X.; Clot, E.; Eisenstein, O.; Boehm, V. P. W.; Roeper, M. *J. Am. Chem. Soc.* **2008**, *130*, 6288.

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