Development of New Olefin Metathesis Catalysts for Applications in the Chemical and Pharmaceutical Industries

Yann Schrodi*,†, Alexandre A. Pletnev,† Thay Ung,† Garik Mkrtumyan,† Donde Anderson,‡ Robert H. Grubbs‡

† Materia, Inc., and ‡ California Institute of Technology

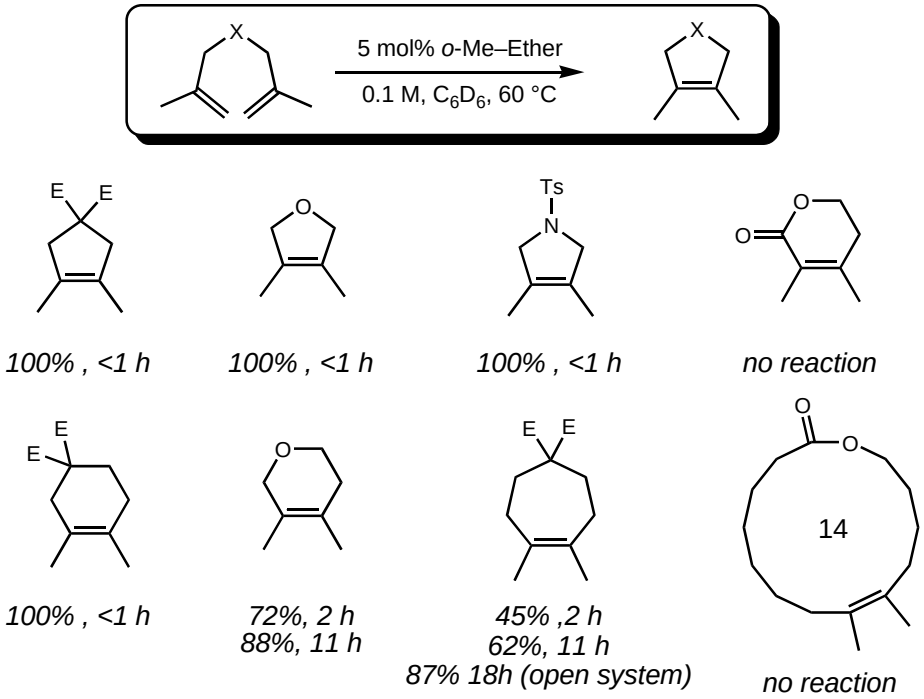
Development of New Catalysts at Materia

Recent Case Studies:

- **Pharmaceutical Interest:**
  - Catalysts for the formation of tetra-substituted olefins via RCM (Ian Stewart's talk)
- **Cargill Collaboration:**
  - Catalysts for the ethenolysis and cross-metathesis of renewable feedstocks (e.g., seed oils)

Catalysts for the Formation of Tetra-Substituted Olefins via RCM

Produced on kg scale
Available from Aldrich



At Materia: Thay Ung; Garik Mkrtumyan

In Grubbs group: Ian Stewart

Used in Brian Stoltz group: David White's talk

materia
CATALYSTS FOR CHANGE

Stewart *et al Org. Lett.* **2007**, *9*, 1589-1592

Ethenolysis of Methyl Oleate: Background

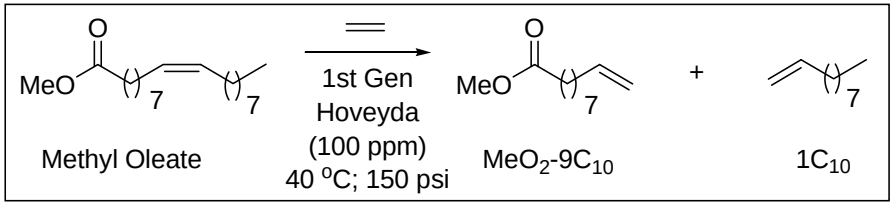
Research Group	Catalyst	TON*
Mandelli [1]	Rhenium	110
Grubbs [2]	1st Gen Grubbs (proof of principle)	140
Warwel [3]	1st Gen Grubbs	3,000
Dow [4]	1st Gen Hoveyda/Grubbs	2,600

* Turn Over Number = moles of ethenolysis products / moles of catalyst

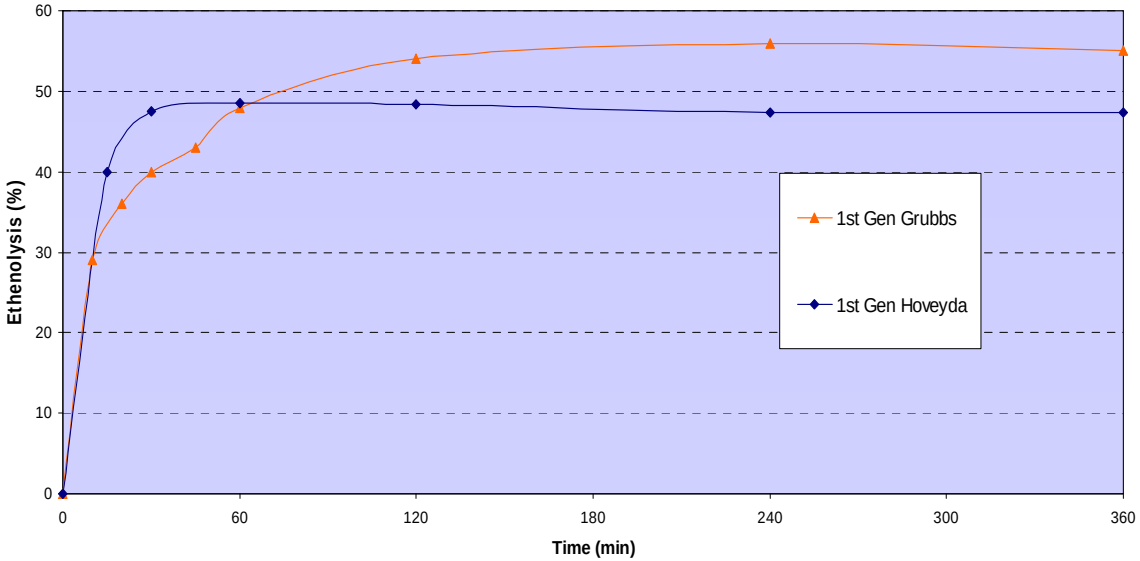
1) *J. Am. Oil Chem. Soc.* **1996**, 73, 229-232
2) Grubbs et al. WO **96**/04289
3) *Chemosphere* **2001**, *43*, 39-48.
4) **02**/076920 A1

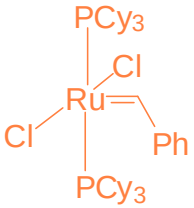
materia
CATALYSTS FOR CHANGE

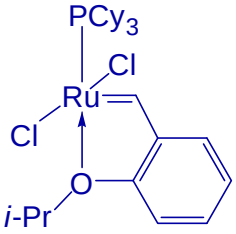
Ethenolysis of Pure Methyl Oleate using 1st Gen Hoveyda Catalyst



Methyl Oleate | MeO_2-$9C_{10}$ | $1C_{10}$



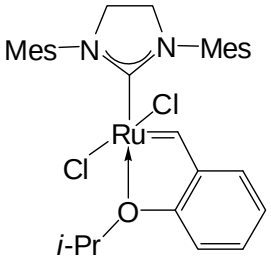


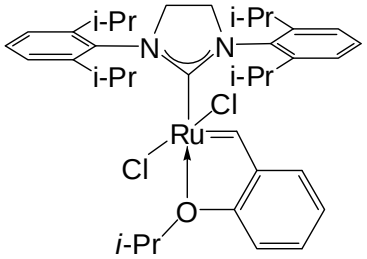


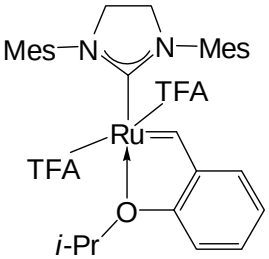
At catalyst loading of 100 ppm: Yield = 48 %; TON = 4,800
1st Gen Hoveyda is slightly faster but gives lower yield than 1st Gen Grubbs.

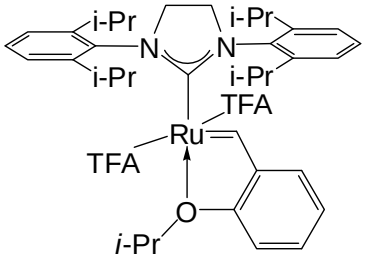
materia
CATALYSTS FOR CHANGE

New Ethenolysis Catalysts









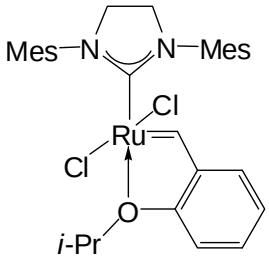
Conversion	60 %	70 %	38 %	49 %
Selectivity	33 %	56 %	71 %	94 %
Yield	20 %	40 %	27 %	46 %
TON	2,000	4,000	2,700	4,600

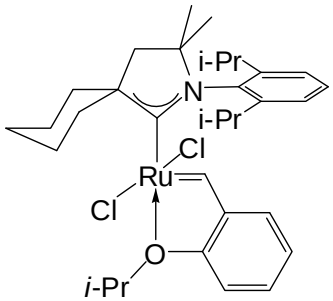
(Conditions: neat MO; 100 ppm catalyst; 40 C; 150 psi ethylene)

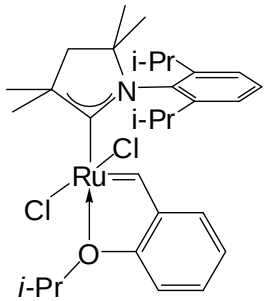
Selectivity for ethenolysis products increases with the size of the NHC and anionic ligands.

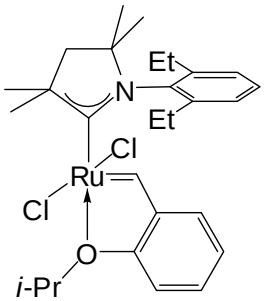
materia
CATALYSTS FOR CHANGE

New Ethenolysis Catalysts









Time	15 min	> 20 hours	> 20 hours	30 min
Conversion	60 %	46 %	61 %	73 %
Selectivity	33 %	94 %	92 %	73 %
Yield	20 %	43 %	56 %	53 %
TON	2,000	4,300	5,600	5,300

(Conditions: neat MO; 40 C; 150 psi ethylene)

At 10 ppm, this catalyst gives 35 % yield, which corresponds to a highest TON to date: 35,000 !

materia
CATALYSTS FOR CHANGE

Anderson *et al Organometallics* **2007**, *submitted*