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Oxorhenium Species in Catalysis

Joe Derosa
3/9/17

75	186.207
Re	
Rhenium	
[Xe]$4f^{14}5d^56s^2$	

Rhenium Facts:

- third-row transition metal (group VII)
- can access oxidation states from -3 to +7
- estimated average concentration of 1 ppb (part per billion) in Earth's crust
- only obtained as a byproduct of refinement of molybdenum and copper ore
- costs $2,750/kg compared to $24,701/kg for palladium (April 2013)

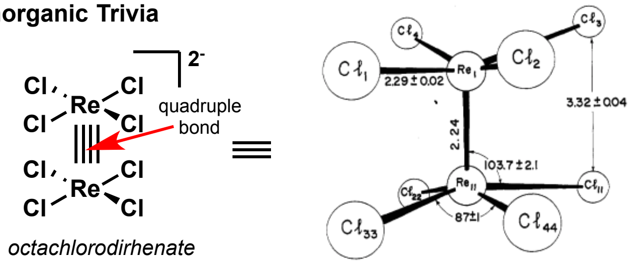
History

- originally discovered by Masataka Ogawa in 1908 and named Nipponium -- discredited due to controversial analysis
- (re)discovered in 1925 by Noddack, Tacke, and Berg in Germany--named "Rhenus" for the river Rhine
- predominantly used for manufacturing of jet engines

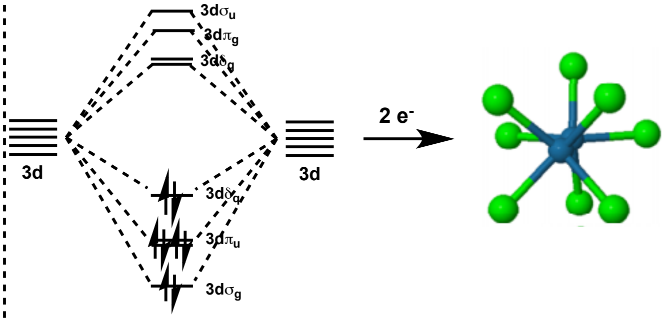
Basic Properties

- third highest melting point (3186 °C) and highest boiling point (5630 °C)
- electropositive
- hexagonal close-packed crystal structure
- fourth densest element at 21.02 g/cm^3

Inorganic Trivia



octachlorodirhenate



- Rhenium complexes are often dimeric and contain quadruple bonding between metal centers, i.e. $Re_2Cl_8^{2-}$
- $Re_2Cl_8^{2-}$ maintains a sterically unfavorable eclipsed geometry due to the rigidity of the δ-bond formed from the overlap of *d* orbitals
- It is also possible for rhenium trimers to exist, but relatively unexplored

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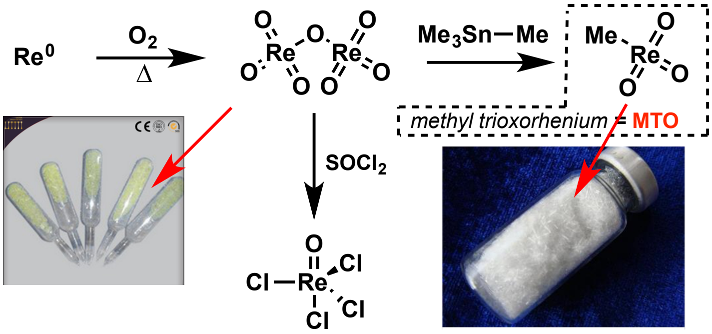
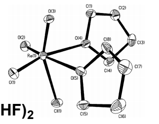
Introduction to Rhenium-oxo Species

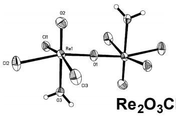
Due to time contraints, the focus of this presentation will be rhenium-oxo species in catalysis. The following classes of transformations will not be detailed herein: (1) olefin disproportionation, (2) olefin metathesis, (3) enyne cyclizations, (4) electrochemical oxidations.



- metallic rhenium can be heated in the presence of O_2 to form a bridged rhenium (VII) oxo dimer that can be used as a supply of starting material for the synthesis of various oxorhenium species
- treatment of Re_2O_7 with HCl, TMSCl, $SOCl_2$, and a variety of temperatures produces chlorooxorhenium in a wide range of oxidation states



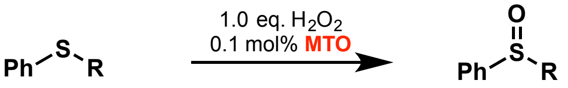
ReO$_3$Cl•(THF)$_2$



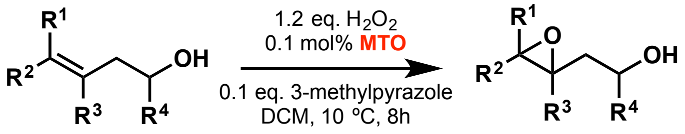
Re$_2$O$_3$Cl$_6$•(H$_2$O)$_2$

Girolami, *Dalt. Trans.* **2007**, 675.

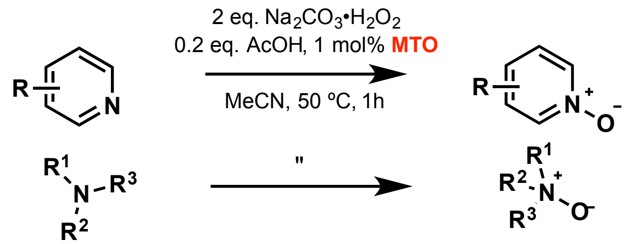
Oxygen Atom Transfer with MTO



Yamazaki, *Bull. Chem. Japan* **1996**, *69*.

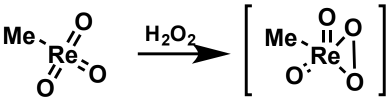


Yamazaki, *J. Org. Chem.* **2012**, *77*, 9884-9888.



Sain and coworkers, *Synlett* **2006**, 2661-2663.

- For examples involving imines, see Goti, *Org. Lett.* **2007**, *9*, 473-476.



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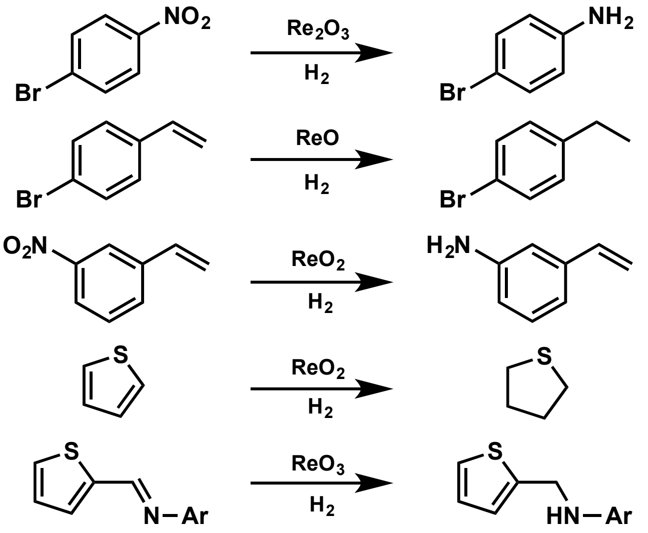
Selected Hydrogenation Examples

- The degree of selectivity depends on the substrate and oxidation state of the oxorhenium species employed: (1) *higher* oxides are generally less effective in reducing aromatics, (2) *lower* oxides react faster with alkenes



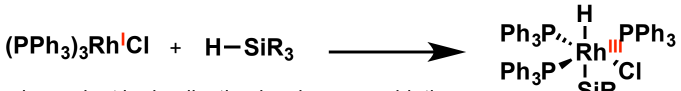
NO_2 > CO > CH=N > C=C > C–C >> C–S >>C–X
general order of sensitivity

Broadbent, "Rhenium and its Compounds as Hydrogenation Catalysts" **1967**.

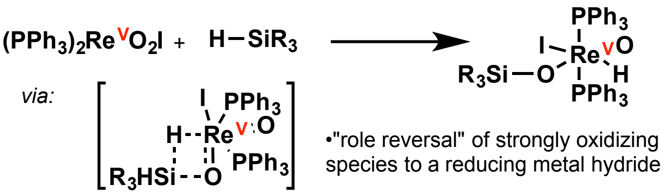
Evolution of Oxorhenium Catalysts

- In 2003, Toste and coworkers set out to "reverse the role" of metal-oxo π-bonds for chemoselective catalytic reductions of aldehydes using a rhenium(V)-dioxo complex

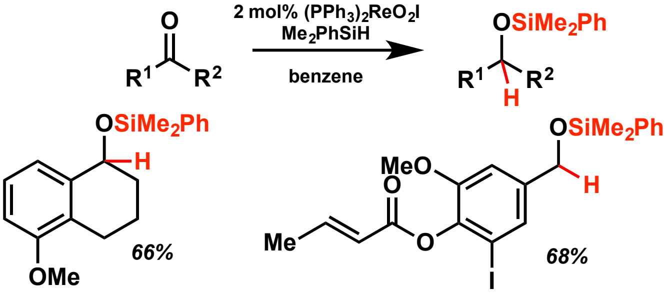
Toste, *J. Am. Chem. Soc.* **2003**, *125*, 4056.



- low valent hydrosilyation involves an oxidative addition step



- "role reversal" of strongly oxidizing species to a reducing metal hydride



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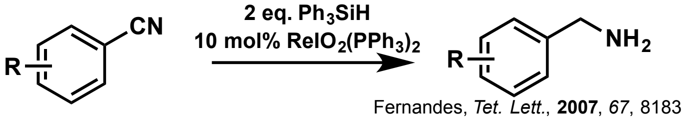
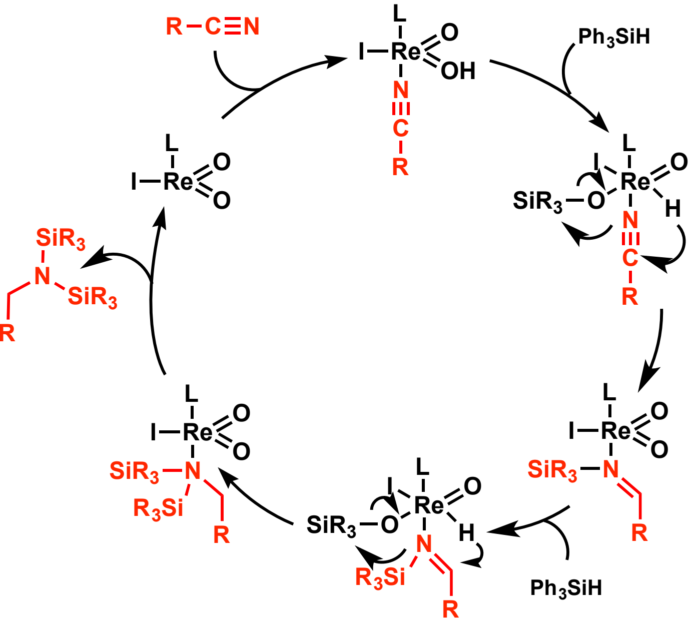
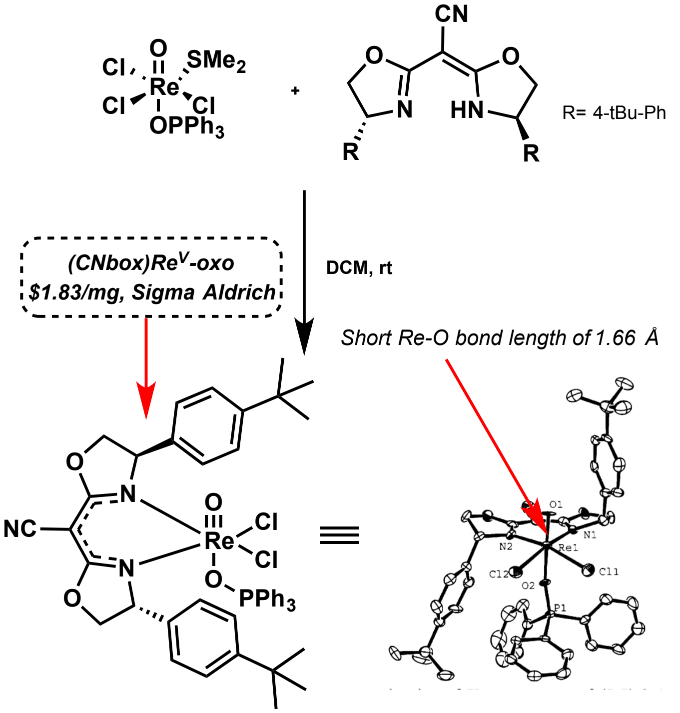


Fernandes, *Tet. Lett.*, **2007**, *67*, 8183.



- For oxorhenium-catalyzed reductions of sulfoxides, alkenes, nitroarenes, and reductive amination of aldehydes: Fernandes, *J. Org. Chem.*, **2009,** *74*; Fernandes, *Tetrahedrom Lett.*, **2010**, *51*.; Fernandes, *Adv. Synth. Catal.*, **2009**, *352*.



(CNbox)Re^{V}-oxo
\$1.83/mg, Sigma Aldrich

Short Re-O bond length of 1.66 Å

- Toste and coworkers performed mechanistic studies on previous work, carbonyl reduction, and observed necessity for neutral ligand dissociation
- Sought to make a chiral ligand capable of asymmetric transformations, monodeprotonated BOX ligands were tested

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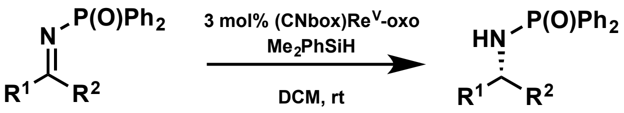
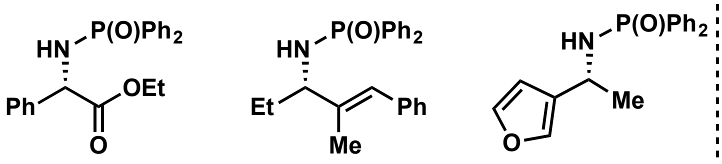


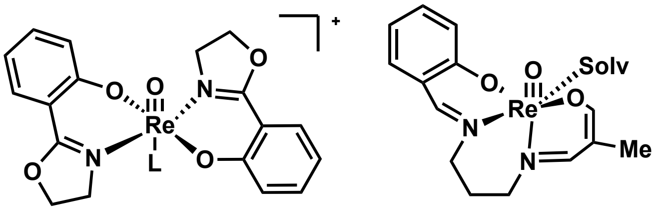


83%, >99% ee *71%, >99% ee* *76%, 99% ee*

- Interestingly, compounds whose equilibrium favor the enamine tautomer undergo the reaction in high yield and ee
- *p*-methoxyphenyl (PMP) imines could also serve as competent substrates
- aliphatic imine substrates proceeded with poor enantiocontrol

Toste, *J. Am. Chem. Soc.* **2005**, *127*, 12462.

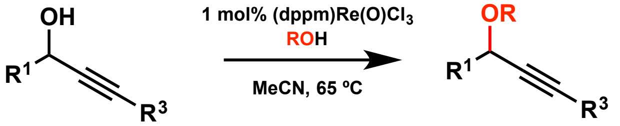
Other oxorhenium complexes:



Abu-Omar, *J. Am. Chem. Soc.* **2005**, *127*, 15374.

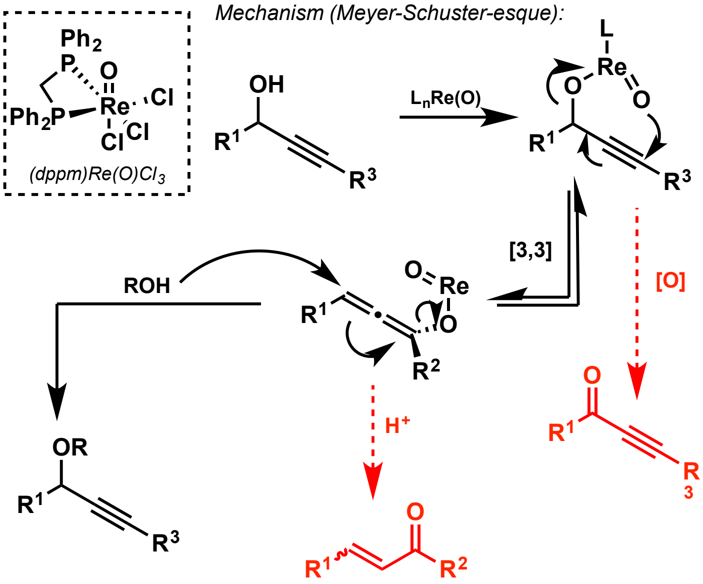
- For asymmetric reduction of ketones using chiral (CNbox) ligands, see Toste, *Chem.– Eur. J.*, **2010**, *16*, 9555.

C–C, C–O and C–N Bond Forming Reactions



(dppm)Re(O)Cl$_3$

Mechanism (Meyer-Schuster-esque):



Toste, *J. Am. Chem. Soc.* **2003**, *125*, 6076.

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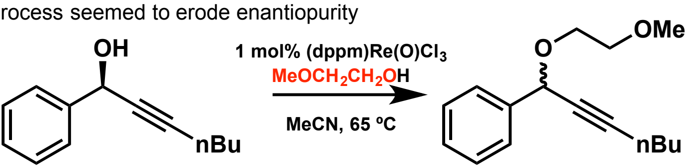
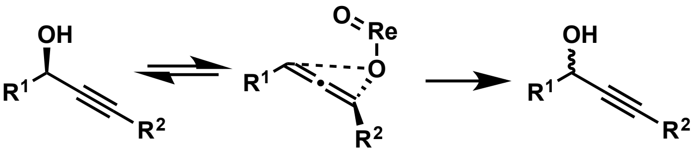
- Based on the proposed mechanism, the chiral allene intermedaite was hypothesized to be indicative of a stereospecific process; however, the process seemed to erode enantiopurity



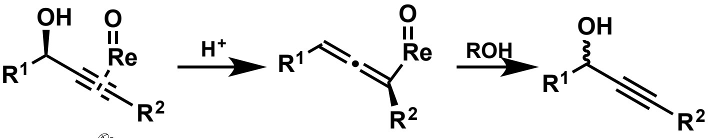
86% ee *0% ee*

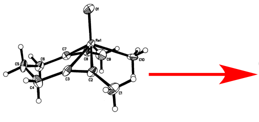
Potential Rationalization (1) - 1,3 oxygen shift catalyzed by oxorhenium



Gordon, *Organometallics* **1998**, *17*, 1835.

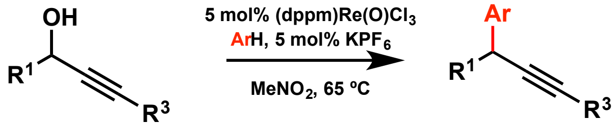
Potential Rationalization (2) - Rhenium-alkyne complexation





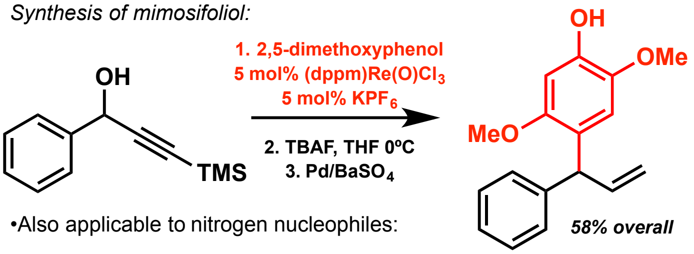
diyne-oxorhenium complex

Norton, *Inorg. Chem.* **2001**, *40*, 2942.



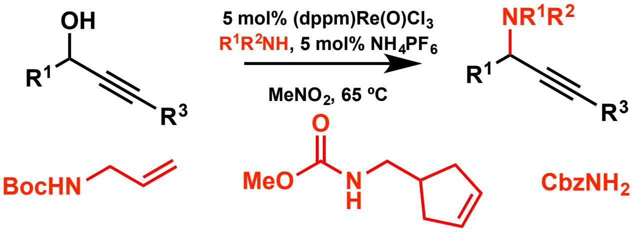
- Aryl nucleophiles and other carbon nucleophiles required the use of catalytic hexafluorophosphate to sequester chloride ligand from rhenium
- Hypothesized to ease chelation of propargyl alcohol and favor allene intermediate
- Methodology also extended to include allylation *via* allyltrimethylsilane, see: Toste, *J. Am. Chem. Soc.* **2003**, *125*, 15761.

Synthesis of mimosifoliol:



58% overall

- Also applicable to nitrogen nucleophiles:



Toste, *Org. Lett.* **2005**, *7*, 2503.

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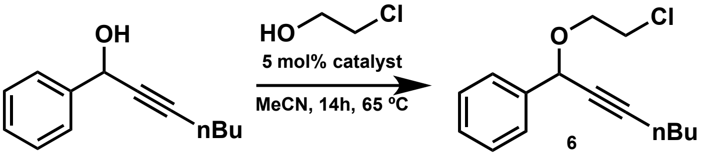
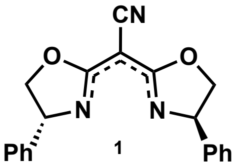
Performance of other metals:

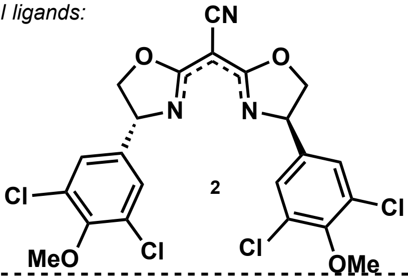


entry	catalyst	% enone	% ketone	%6
1	$V(O)(acac)_2$	0	29	19
2	$[Mo_2O_7(BINOL)_2](NBu_4)_2$	0	10	15
3	$MoO_2(acac)_2$	20	trace	77
4	$(catechol)ReOCl_3$	77	0	25
5	$(dppm)ReOCl_3$	trace	trace	96

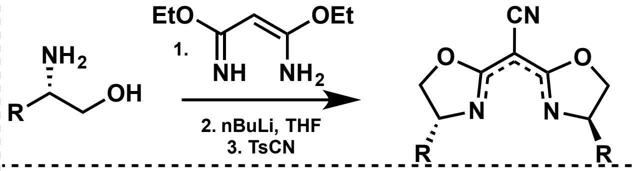
- $MoO_2(acac)_2$ was found to only perform well for 1° alcohols

Selected examples of new chiral ligands:

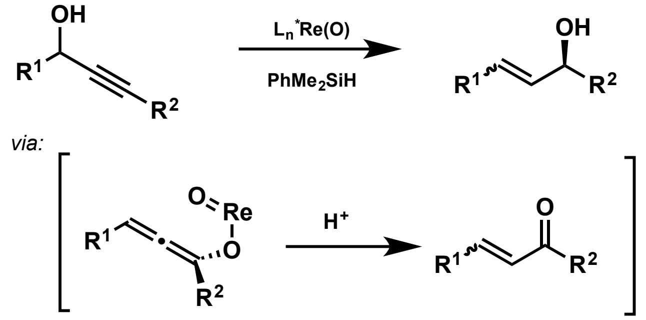

1


2

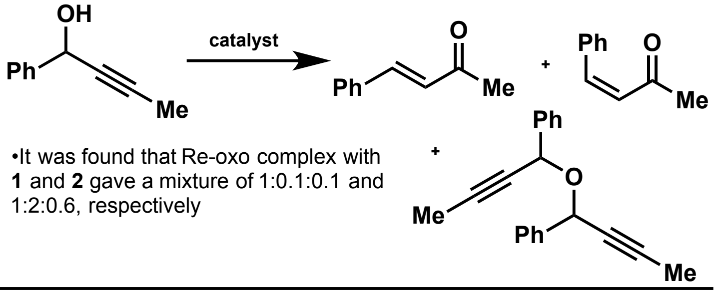
Synthesis of (CNbox) ligands



Tandem Meyer-Schuster-hydrosilyation:



- Initial results showed that traditional (CNbox) chiral oxorhenium complexes gave a mixture of products



- It was found that Re-oxo complex with **1** and **2** gave a mixture of 1:0.1:0.1 and 1:2:0.6, respectively

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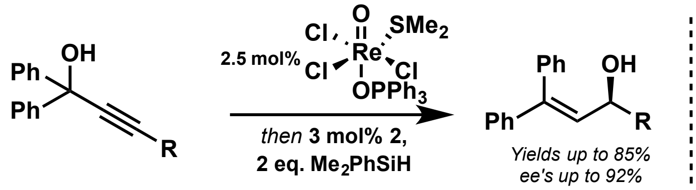
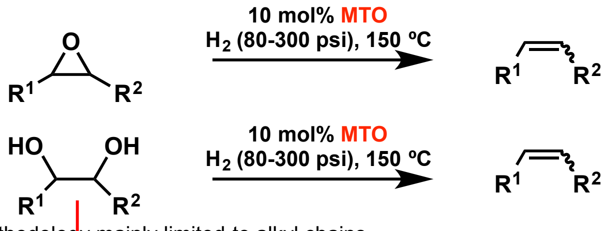


Yields up to 85%
ee's up to 92%

- Reaction also applied to allenyl alcohols and realized with similar success

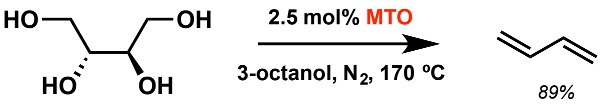
Deoxygenation of Diols and Epoxides



- Methodology mainly limited to alkyl chains

Abu-Omar, *Inorg. Chem.* **2009**, *48*, 9998.

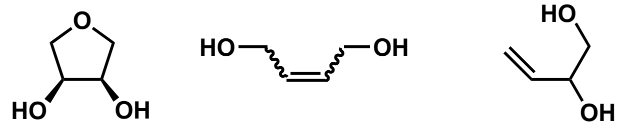
*mechanism involves a **deoxydehydration (DODH)** step!*

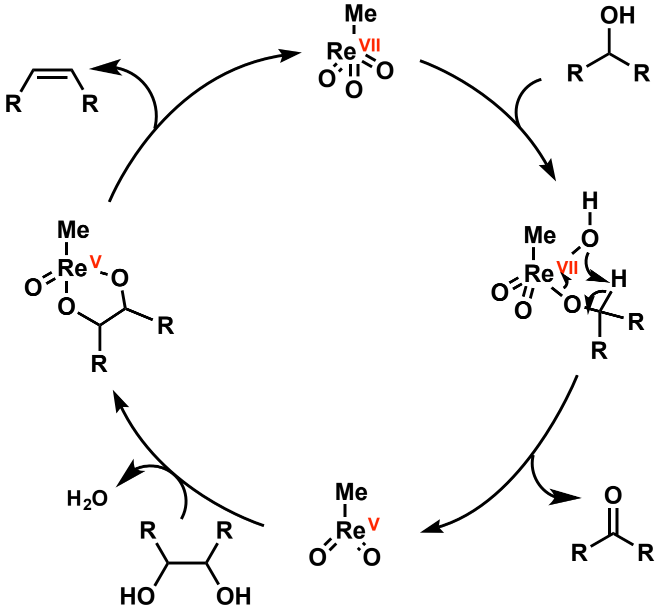


89%

Toste, *ACIEE* **2012**, *51*, 8082.

Not observed:





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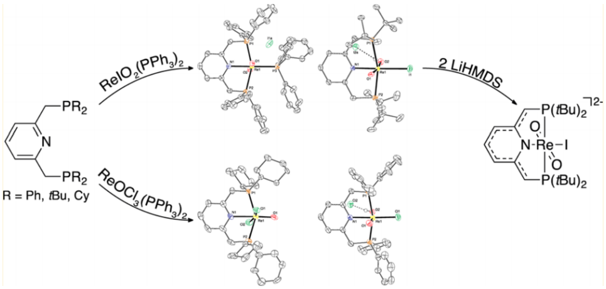
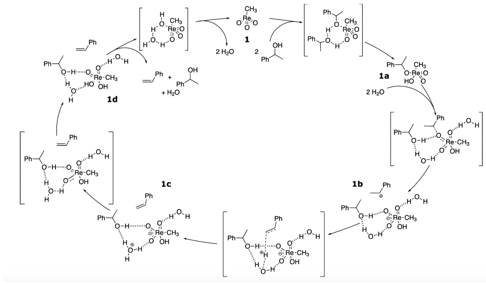


Gebbink, *Organometallics* **2014**, *33*, 2201-2209.

- Attempts have been made toward involving pincer ligands in oxorhenium catalysis using PNP-connectivity for DHDO reactions, for pincer-rhenium complexes competent in electrochemical oxidation see: Peruzzini, *Inorg. Chim. Acta* **2002**, *327*, 140.

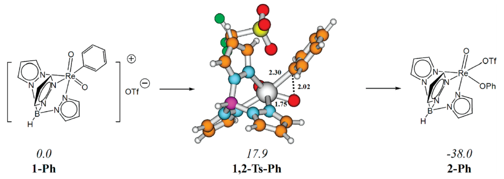
- Ultimately, both PNP-oxorhenium species failed as competent catalysts for oxygen atom transfer under both oxidizing conditions in the presence of an alkene and *N*-oxide abstraction -- thought to be noninnocent when deprotonated for dehydration reactions



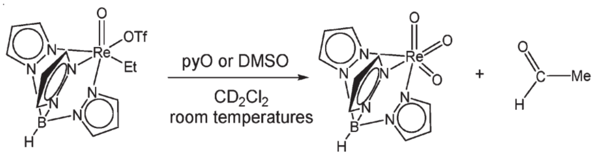
Gebbink, *ACS Catal.* **2015**, *5*, 281-300.

C–O Bond Formation from Rhenium-Oxo Alkyl Complexes

- For the full paper, see Goddard, III *Organometallics* **2010** *29*, 2026-2033.



- In the case of phenyl substituted complex, the final phenoxide is thought to form by an aryl migration mechanism -- however, an analgous ethyl substitution yielded acetaldehyde



Possible Pathway (1) - Ethyl 1,2-migration

- This would be the parallel mechanism to the initial phenoxide result
- DFT calculations suggested that the reaction barrier of the migration was only 22.1 kcal/mol -- only 4.2 kcal/mol higher than phenyl case!

Experiment: Independent synthesis of $(HBpz_3)ReO(OEt)OTf$ and exposure to reaction conditions -- generates acetaldehyde AND ethanol!

indicates that there is another lower energy pathway!

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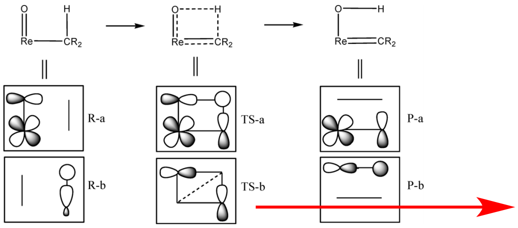
Possible Pathway (2) - α– or β–Hydrogen Abstraction by Oxo

(a) *α–Hydrogen Abstraction by Oxo*

- The formation of a Re-ethylidene would require 44.9 kcal/mol to overcome, making it thermally inaccesible

Explanation: Molecular orbital analysis throughout the course of the reaction suggests that no molecular orbitals remain both bonding and orthogonal in transition state

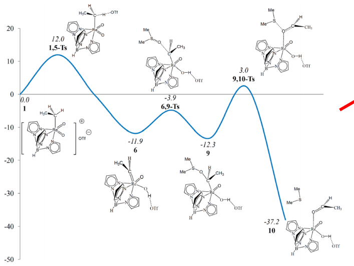


"2+2 forbidden"

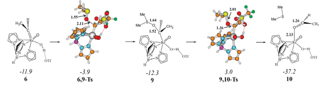
(b) *β–Hydrogen Abstraction by Oxo*

- Reaction barrier of the process is only 8.0 kcal/mol lower than (a)

indicates that there is another lower energy pathway!

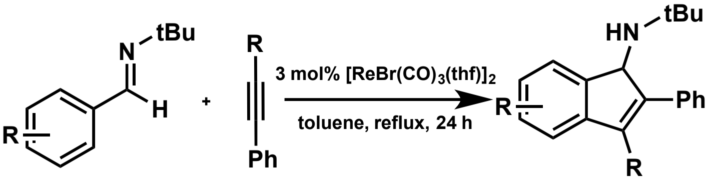


Triflate assisted H-abstraction followed by DMSO oxygen transfer!



C–H Functionalization

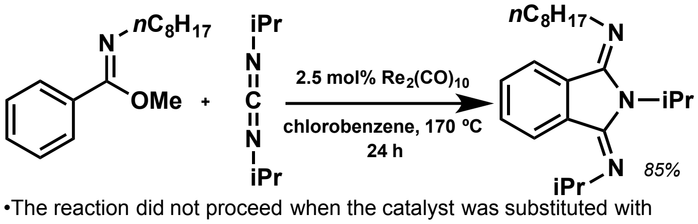
- In nearly every C–H activation/functionalization, optimization tables show that oxorhenium species are not competent catalysts for the intended transformation
- This section will focus only on $C(sp^2)$–H bonds, for $C(sp^3)$–H bonds see: Hartwig, *ACIEE* **1999**, *38*, 3390-3392.



Yields as high as 99%

- Takai and coworkers observed low yield when using a pentacarbonyl rhenium species and no reactivity under CO pressure - *why?*

Takai, *J. Am. Chem. Soc.* **2005**, *127*, 13498-13499.



- The reaction did not proceed when the catalyst was substituted with $Pd(OAc)_2$, $RhCl(PPh_3)_3$, $Cu(OAc)_2$, and only proceed in 16% with $[Cp^*IrCl_2]_2$

Kuninobu, *Org. Lett.* **2016**, *18*, 2459-2462.