Due to cyclizations, detailed species produces rhenium.

**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
- 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/cm³

**Oxorhenium Species in Catalysis**

**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 O₂ 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 Re₂O₇ with HCl, TMSCl, SOCl₂, and a variety of temperatures produces chlororoxorhenium in a wide range of oxidation states

**Inorganic Trivia**

- Rhenium complexes are often dimeric and contain quadruple bonding between metal centers, i.e. Re₂Cl₆²⁻
- Re₁Cl₄²⁻ maintains a sterically unfavorable eclipsed geometry due to the rigidity of the σ-bond formed from the overlap of σ orbitals
- It is also possible for rhenium trimers to exist, but relatively unexplored

**Oxygen Atom Transfer with MTO**

1.0 eq. H₂O₂
0.1 mol% MTO


1.2 eq. H₂O₂
0.1 mol% MTO

0.1 eq. 3-methylpyrazole
DCM, 10 °C, 8h


2 eq. Na₂CO₃•H₂O₂
0.2 eq. AcOH, 1 mol% MTO

MeCN, 50 °C, 1h

Sain and coworkers, Synlett 2006, 2661-2663.

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

**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.

\[
(PPh_3)_3Rh^{+}Cl + HSiR_3 \rightarrow Ph_3P\overset{\text{Me}}{\text{Rh}}PPh_3 Cl^{-} Ph_3P^{+} SiR_3
\]

• low valent hydrosilylation involves an oxidative addition step

\[
(PPh_3)_3Re^{V}O_2Cl + HSiR_3 \rightarrow \text{Me}_2\text{PhSiH}^+ \rightarrow \text{Ph}_3P^{+} \overset{\text{SiMe}_2\text{Ph}}{\text{O}} SiMe_2Ph
\]

via:

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

---

**Oxorhenium Species in Catalysis**


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Oxorhenium Species in Catalysis

Joe Derosa 3/9/17


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

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

Potential Rationalization (2) - Rhenium-alkyne complexation

Also applicable to nitrogen nucleophiles:
Performance of other metals:

<table>
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<tr>
<th>entry</th>
<th>catalyst</th>
<th>% enone</th>
<th>% ketone</th>
<th>%6</th>
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<td>1</td>
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<td>19</td>
</tr>
<tr>
<td>2</td>
<td>[MoO₂₂(BINOL)]₃(NBu)₂</td>
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<td>15</td>
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<td>3</td>
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<td>trace</td>
<td>77</td>
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<tr>
<td>4</td>
<td>(catechol)ReOCl₃</td>
<td>77</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>(dpmm)ReOCl₃</td>
<td>trace</td>
<td>trace</td>
<td>96</td>
</tr>
</tbody>
</table>

• MoO₂(acac)₂ was found to only perform well for 1° alcohols

Tandem Meyer-Schuster-hydrosilylation:

\[
\begin{align*}
\text{R}^1\text{R}^2\text{R}^3 & \xrightarrow{\text{L}^n\text{Re(O)}} \xrightarrow{\text{PhMe}_2\text{SiH}} \text{R}^1\text{R}^2\text{R}^3 \\
\text{via:} & \\
\xrightarrow{\text{H}^+} & \xrightarrow{\text{H}^+} \\
\text{R}^1\text{R}^2\text{R}^3 & \xrightarrow{\text{R}^1\text{R}^2\text{R}^3} \text{R}^1\text{R}^2\text{R}^3
\end{align*}
\]

Selected examples of new chiral ligands:

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

Synthesis of (CNbox) ligands:

• 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

Deoxygenation of Diols and Epoxides:

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

Not observed:

• Methodology mainly limited to alkyl chains


\[\text{Toste, ACIEE 2012, 51, 8082.}\]
**Oxorhenium Species in Catalysis**

**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 phenoxy is thought to form by an aryl migration mechanism -- however, an analogous ethyl substitution yielded acetaldehyde.

[Diagram showing the reaction]

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

- This would be the parallel mechanism to the initial phenoxy 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)ReO(OEt)OTf and exposure to reaction conditions -- generates acetaldehyde AND ethanol!

indicates that there is another lower energy pathway!

---

**Oxorhenium Species in Catalysis**

**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 inaccessible

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

(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!

---

**C–H Functionalization**

- In nearly every C–H activation/functionlization, optimization tables show that oxorhenium species are not competent catalysts for the intended transformation

This section will focus only on C(sp2)–H bonds, for C(sp3)–H bonds see: Hartwig, ACIEE 1999, 38, 3390-3392.

[Diagram showing the reaction]

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


- The reaction did not proceed when the catalyst was substituted with Pd(OAc)2, RhCl(PPh3)3, Cu(OAc)2, and only proceed in 16% with [Cp*IrCl2]2

indicates that there is another lower energy pathway!