

Thorium Energy Alliance

7th Annual Future of Energy Conference

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Thorium's Bright Lights: An Overview of Thermally Driven Catalysis

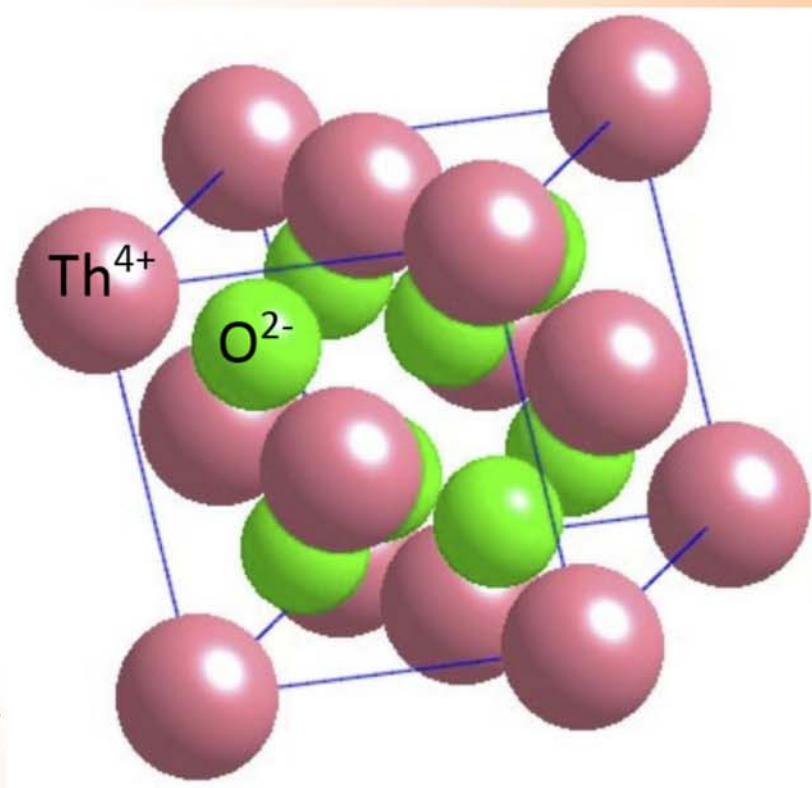
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Blue Point, NY 11715

Outline

- A Brief Review:
 - Catalysis in general
 - Metal-driven catalysis
- ThO_2 – crystallographic and structural considerations
 - Brief comparison with TiO_2
- AnO_2 ; An = U, Th: challenging catalysis chemistry
- Organoactinidic catalysis (An = Th, U):
 - Highly regioselective
 - Highly enantioselective and with high yields

Thorium Dioxide (Thoria) ThO_2 : the “First” Catalyst: Crystallographic and Structural Considerations

- Cubic (fluorite)^{1,2}
- $\cdot Fm\bar{3}m$
 - $a=5.586\text{\AA}$.
 - MP: $\sim 3300^\circ\text{C}$.
- Isomorphous and completely soluble with UO_2 , NpO_2 , PuO_2 , AmO_2 ¹



¹Rough, F.A., Bauer, A.A. BMI-1300 Constitution of Uranium and Thorium Alloys 1958 13th ed. Review. Battelle Corporation

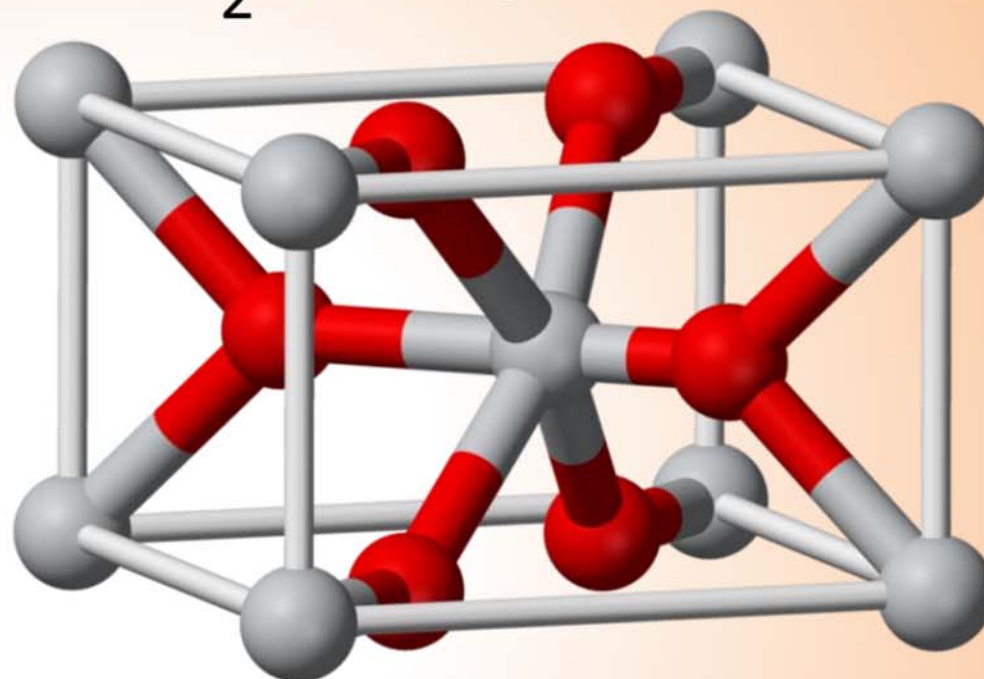
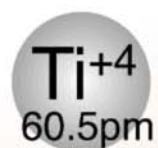
²Patnaik, P. Handbook of Inorganic Chemicals. McGraw Hill 2003.

Titanium Dioxide TiO_2 (comparison)

- Also widely used in hydrogenation
- C^{sp^3} - C^{sp^3} oxidation
and esterification catalysis^{1,2}
- Rutile (cartoon right) and anatase phases
- $P4/mnm$

– $a = 4.6966\text{\AA}$

– $c = 3.3091\text{\AA}$

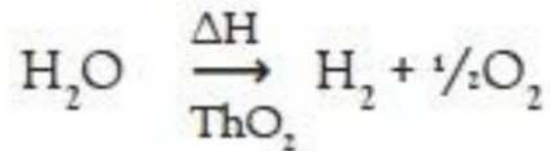


¹McNeff, C.V., McNeff, L.C., Yan, B., Nowlan, D.T., Rasmussen, M., Gyberg, A.E., Krohn, B.J., Fedie, R.L., Thomas R. Hoyer, T.R. Appl. Cat. A: Gen. 343 (2008) 39–48

²Nylén, U. KTH – Ring-opening Catalysts for Cetane Improvement of Diesel Fuels The Royal Institute of Technology SE-100 44 Stockholm, Sweden

Thorium Dioxide (Thoria) ThO_2 : the “First” Catalyst

- First record of ThO_2 usage as catalyst as early as 1913¹.
 - Organometallic catalysis (olefinic hydrogenation)
 - Splitting water: H_2O



¹Ellis, Carleton. The Hydrogenation of Oils, Catalyzers and Catalysts and the Generation of Hydrogen and Oxygen. Van Nostrand & Co, 1919

Hydrogenation and Dehydrogenation

- Extensive use of ThO_2 and with mixed oxides from 1914 – 1957:
 - First catalyst used in Fischer Tropsch synthesis^{2,3}
 - Subsequent usage in FT when combined with TiO_2 , ZrO_2 , RhO_2 , CoO_2 ³
 - ThO_2 used in first coal-to-liquids experimental chemistries¹

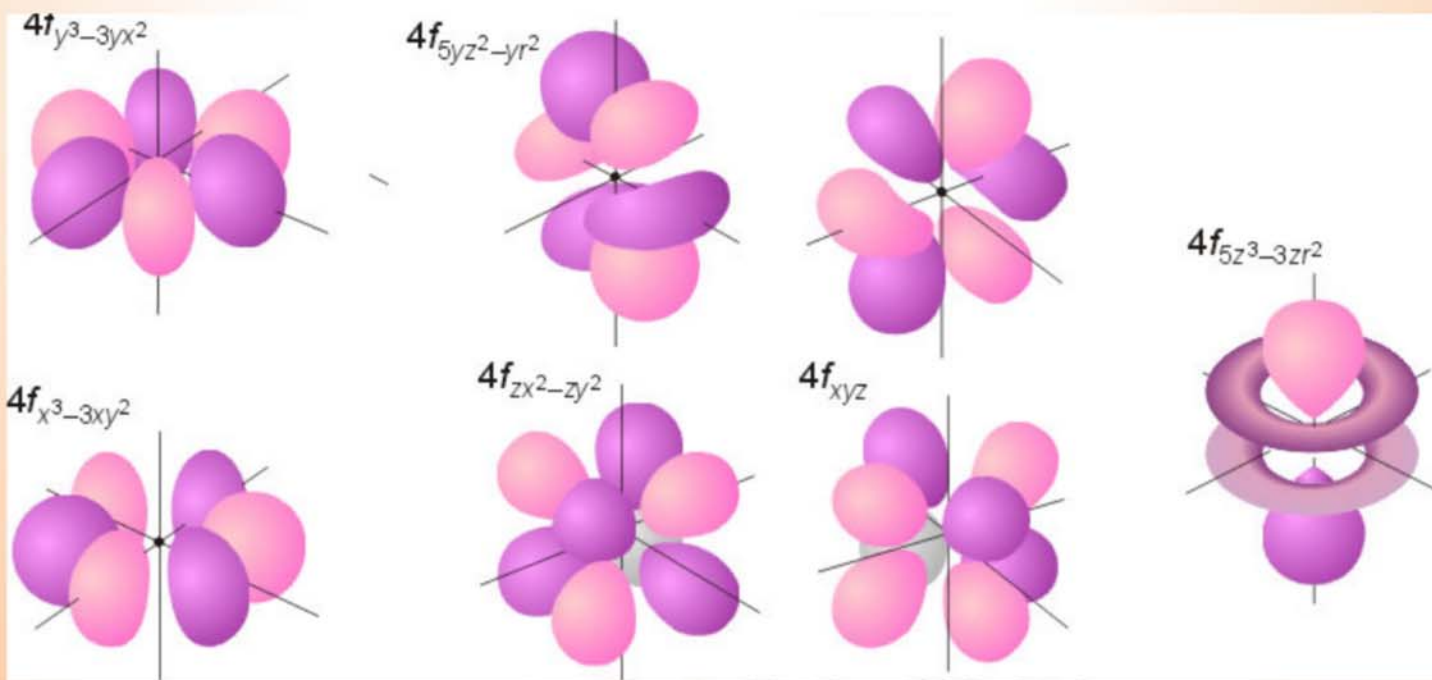
¹H. Pichler, O. Roelen, F. Schnur, W. Rottig, H. Kölbel, Kohlenoxidhydrierung, in: Ullmanns Enzyklopädie der Technische Chemie, 3rd ed., (9), Urban a. Schwarzenberg 1957, p. 685

²F. Fischer, K. Meyer, Brennstoff-Chem. 12 (1931) 225.

³F. Fischer, H. Koch, Brennstoff-Chem. 13 (1932) 61.

What Makes Actinide Catalysis so Interesting?

- Energetics play a major role in the increased availability of the 5f orbitals in the Actinide Series for catalysis.
- D-orbital oxidized cations such as Thorium and Uranium expose 5f Orbitals, such that chemical interaction can occur along a range of molecular geometric configurations (e.g., a wide range of molecules).
- D-F hybridization for both LUMO and HOMO readily occurs



Mixed Actinide oxide-mediated Catalysis: Challenging Chemistry

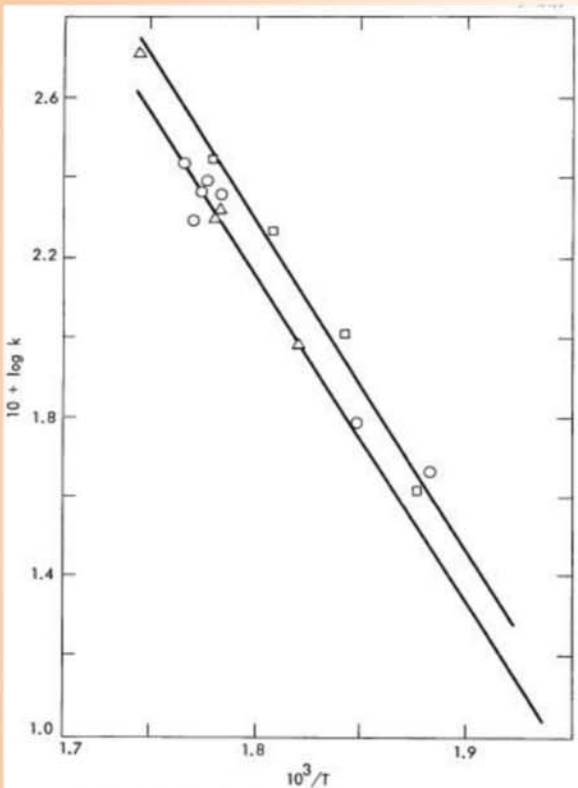


Fig. 18. Arrhenius plots for hydrogen-oxygen reaction catalyzed by thorium oxide calcined at: \circ , 650°; \square , 800°; Δ , 1000°; k in moles/p.s.i.-hr.-m.².

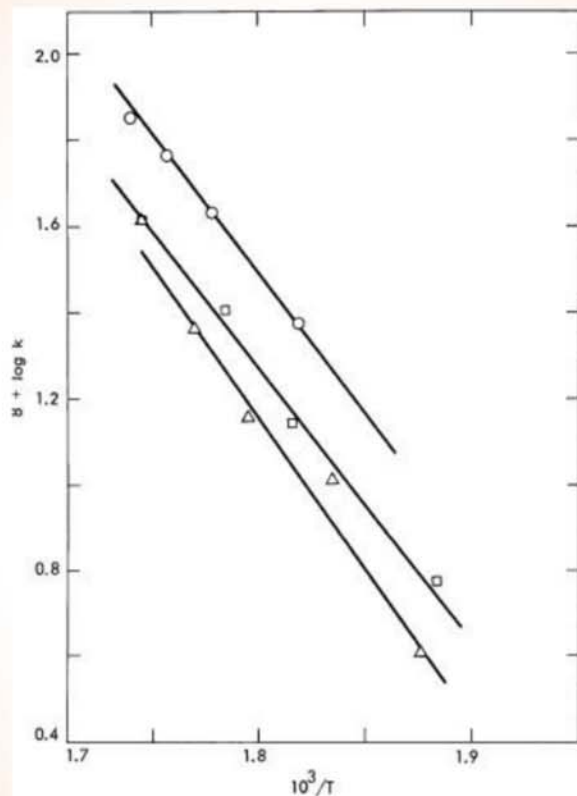


Fig. 19. Arrhenius plot for hydrogen-oxygen reaction catalyzed by thorium-uranium oxide mixed crystals, calcined at: \circ , 650°; \square , 800°; Δ , 1000°; k in moles/p.s.i.-hr.-g.

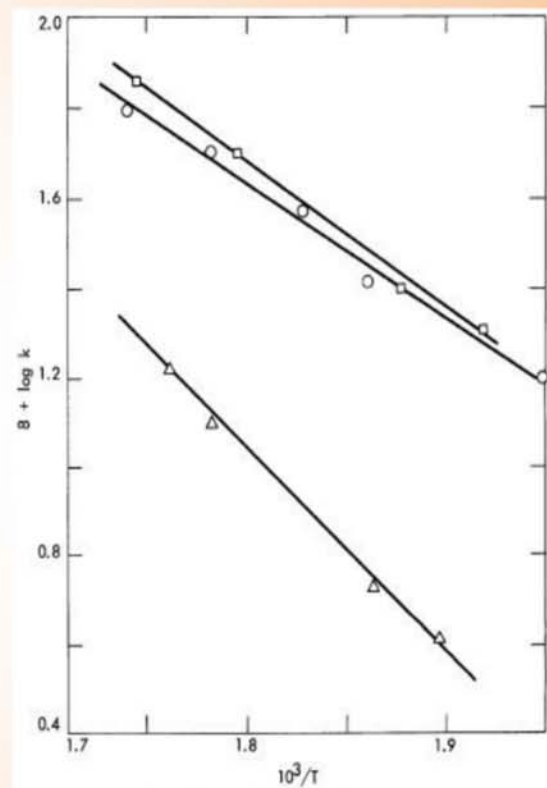


Fig. 20. Arrhenius plot for hydrogen-oxygen reaction catalyzed by thorium oxide with adsorbed uranium oxide calcined at: \circ , 650°; \square , 800°; Δ , 1000°; k in moles/p.s.i.-hr.-g.

Actinide oxide-mediated Catalysis: Challenging Chemistry

- Presence of UO_2 with ThO_2 adsorbed with UO_2 (e.g., Thorianite) for aqueous splitting of water increased ThO_2 catalytic energy required ($\sim 12.1\text{kJ/mol}$ [2.9kcal/mol]).
- Higher calcining temp (1000°C), ThO_2 alone does best
- **Per unit surface area**, however, ThO_2 with UO_2 adsorbed (Thorianite) performed 6x better.

Krohn, N.A. The Catalysis of the Hydrogen-Oxygen Reaction by Aqueous Slurries of Thorium Oxide and Thorium-Uranium Oxide 1960. Oak Ridge National Laboratory ORNL 2878

Organoactinidic Catalysis

- Very advanced organic syntheses
- Highly valuable for pharmaceutical and industrial chemical industries
- Addition across double bonds and in particular geometries (E, Z; cis, trans, gem, stereoselectivity/chirality).
- Highly selective in moiety addition
 - Thiolation (SH)
 - Hydroamination (NHR')
 - Hydrosilylation (Si-H)

Hydroamination (to cite one example): Why should we care?

- Chiral drug market: \$147b (40% of total drug market)
- 82% of antifungals, hematologics, antibiotics
- 78% of all chemotherapeutics (anticancer)
- 72% of all endocrinologics
- 60% of all cardiologics

Worldwide Sales of Single-Enantiomer Pharmaceutical Products (Final Formulation)

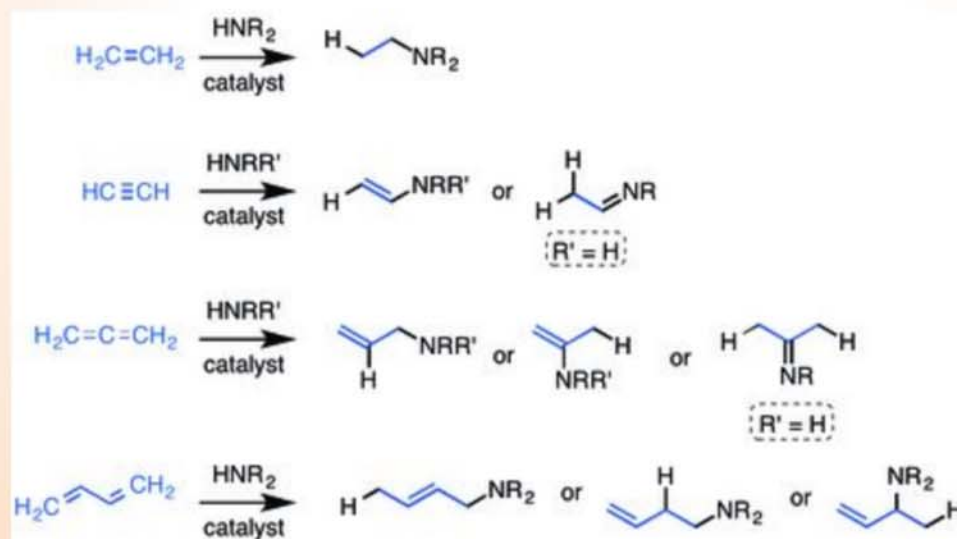
	Total Market (\$ in billions)		Single-Enantiomer (\$ in millions)	
	2000	2001	2000	2001
Cardiovascular	46.6	50.0	27,650	30,169
Antibiotics / Antifungals	31.7	33.0	25,942	26,873
Hormone/Endocrinology	22.0	26.0	15,228	18,474
Cancer Therapy	15.6	17.0	12,201	13,286
Central Nervous System	53.9	55.0	9,322	10,498
Hematology	15.4	16.5	11,989	13,466
Antiviral	19.1	20.0	5,890	6,102
Respiratory	40.5	42.0	6,506	7,875
Gastro-Intestinal	47.2	50.0	4,171	5,411
Ophthalmic	7.4	8.0	2,265	2,434
Dermatological	18.4	18.5	1,272	1,187
Analgesics	23.0	23.5	1,199	1,206
Vaccines	7.3	8.5	3,447	4,299
Other	41.9	42.0	5,929	5,848
Total	390.0	410.0	133,011	147,128

Source: Technology Catalysts International

Challener, C. "Chiral Technologies Put a New Spin on the Fine Chemicals Toolbox" Chem. Mkt. Rep. vol. 262, (21) 2002

Hydroamination

- The addition of an N-H (amine) bond across a C—C double or triple bond, with concomitant C—C oxidation.

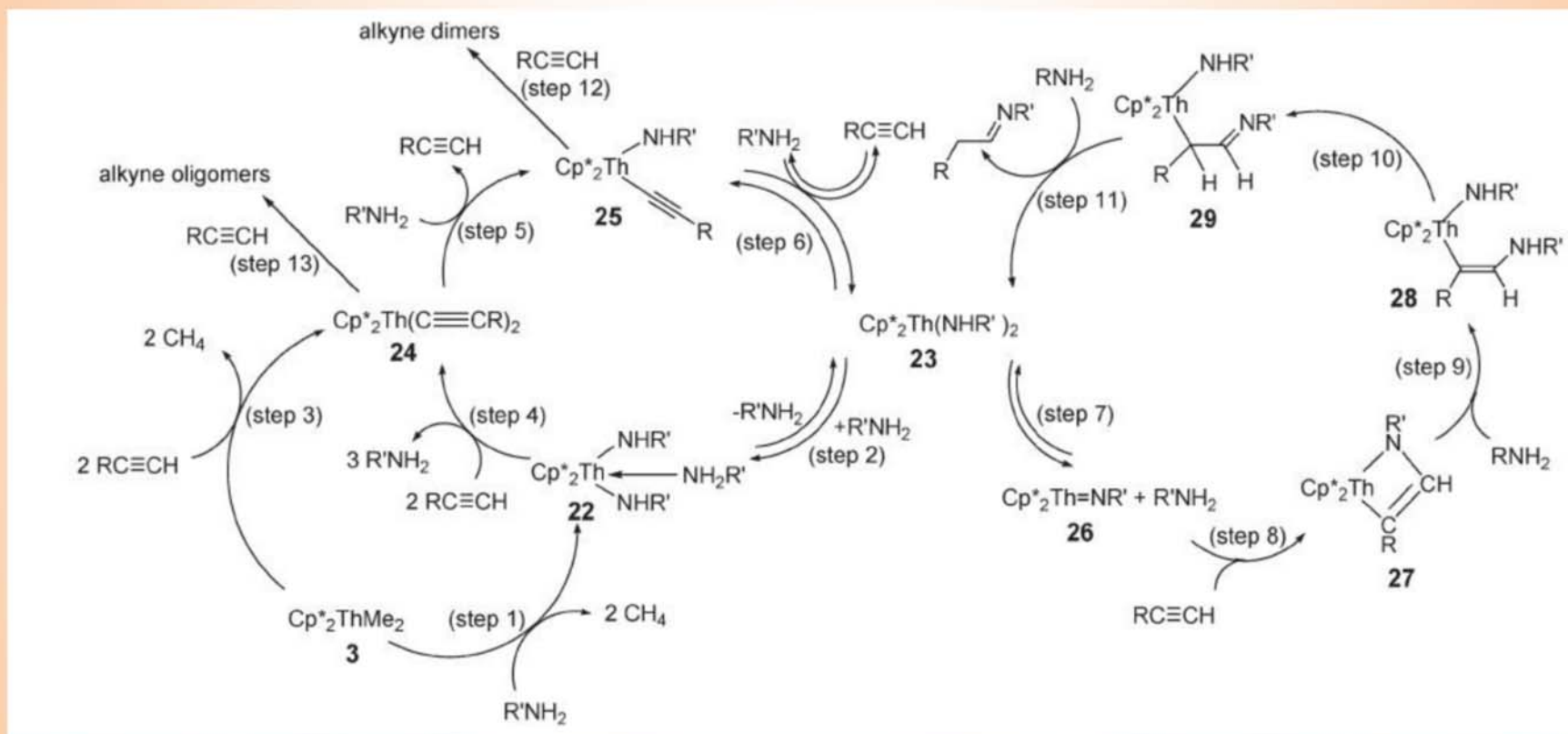


Yvonedep: "General intramolecular hydroamination reactions and their respective products"

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J. Haggin, Chem. Eng. News, 1993, 17, 23

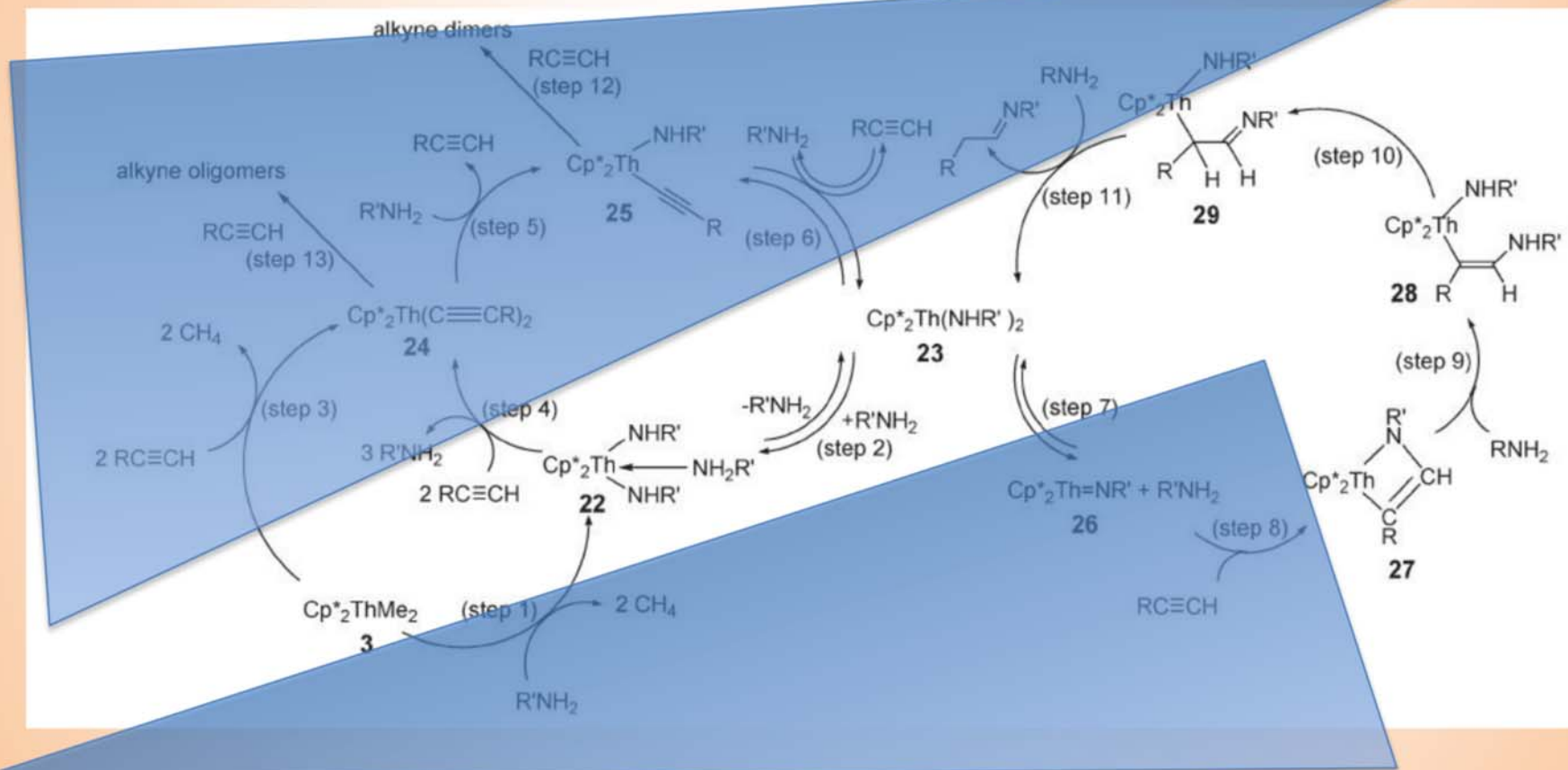
Intermolecular hydroamination (insert laughter here...)



T. Straub, W. Frank, G. J. Reiss and M. S. Eisen, *J. Chem. Soc., Dalton Trans.*, 1996, 2541–2546.

M. S. Eisen, T. Straub and A. Haskel, *J. Alloys Compd.*, 1998, 271–273, 116–122.

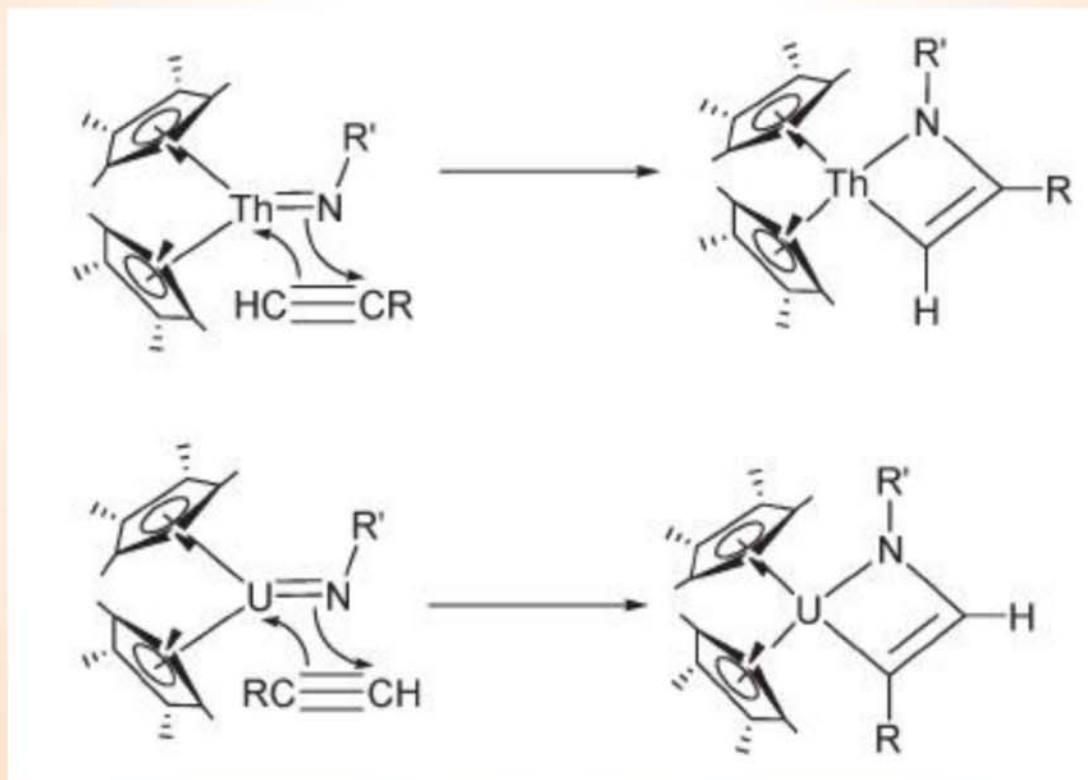
Focusing on key points in reaction mechanism (hydroamination)



T. Straub, W. Frank, G. J. Reiss and M. S. Eisen, *J. Chem. Soc., Dalton Trans.*, 1996, 2541–2546.

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Enantioselective hydroamination very well-mediated by Th, U participation and with high yield



Andrea, T., Eisen, M.S. *Chem. Soc. Rev.*, 2008, 37, 550–567

T. Straub, W. Frank, G. J. Reiss and M. S. Eisen, *J. Chem. Soc., Dalton Trans.*, 1996, 2541–2546.

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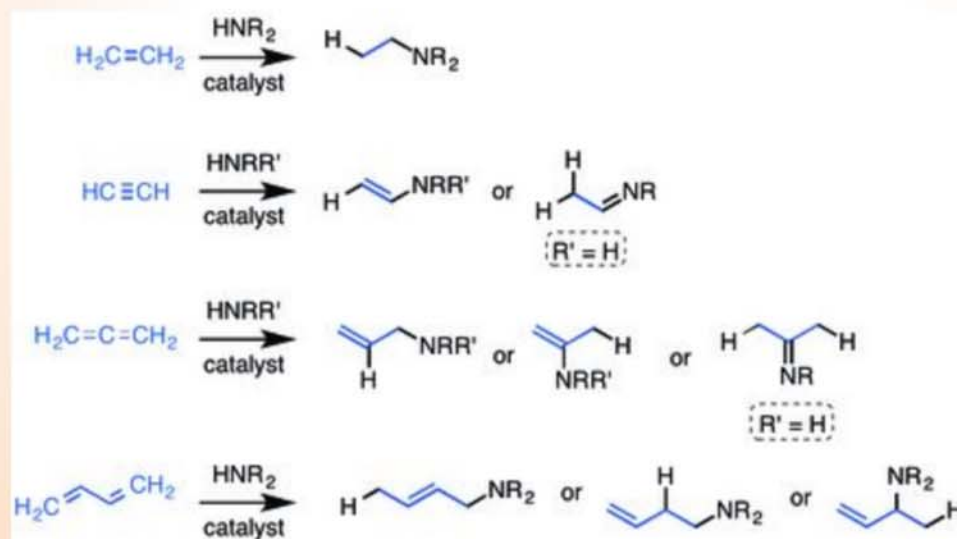
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Conclusions

- Thorium-driven catalysis is over a century old
- Major usage of ThO₂ and UO₂ in the first part of the 20th Century:
 - Water splitting
 - Olefinic hydrogenation
- Mixed oxide catalysis challenging due to several factors:
 - Calcining temperature
 - Solid-solution stoichiometry
 - Deposition methods
- Organoactinidic catalysis continues to explode in growth due to the high regioselectivity and enantioselectivity crucial to pharmaceutical, agricultural and fine-chemical industries