Coordination Chemistry and Reactivity of f Elements

Cours 8: Reactivity, Small Molecule Activation and Catalysis by f-elements

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Coordination Chemistry Group

Learning Objectives

-Know the ability of uranium(III) and Ln(II) complexes to reduce small unreactive molecules (N_2, CO_2)

-Know the possible outcome of these reactions

-Recognize the important effect of the oxophilic character of f elements

-Know the applications of lanthanides in catalysis

-Recognize key lanthanide compounds used in organic reactions

-Suggest reagents for certain transformations

-Recall the main processes involved in actinide and lanthanide catalysis

Principal Applications of Lanthanides in Catalysis

Ln(IV) ions:

- Oxidation by Ce(IV).

Ln(III) ions:

- Lewis acid catalysis by Ln^{3+} :$[Ln(OTf)_3]$
- Hydroelementation reactions. (Insertion of alkenes/alkynes, etc into Ln-E bonds).

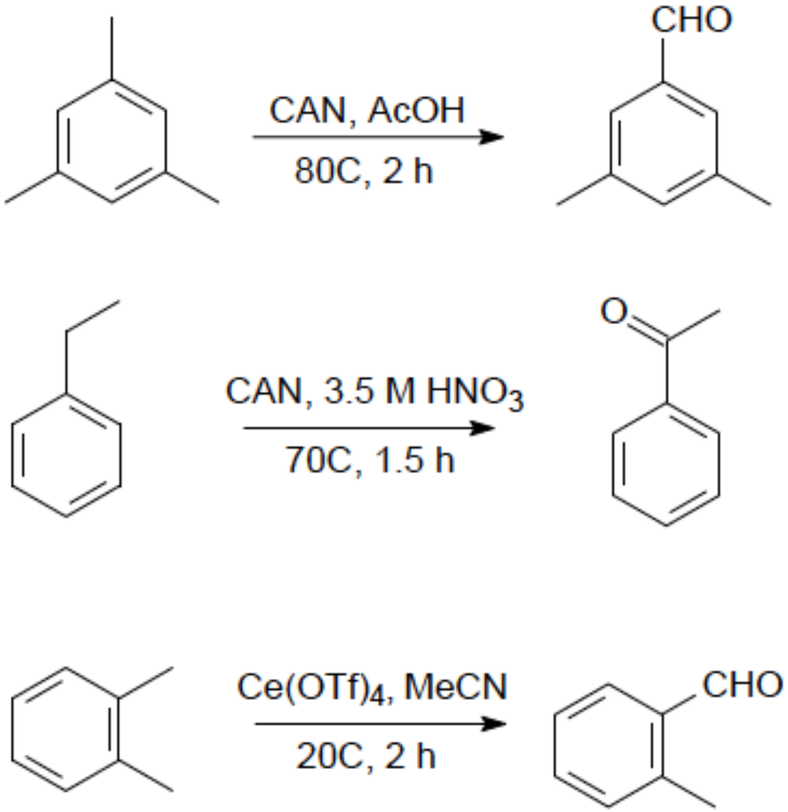
Ln(II) ions:

- One-electron reductions by classical Ln(II) [Ln = Sm, Yb]: SmI_2 (pioneered by Kagan).

Oxidations

Eo [Ce(III)/Ce(IV)] = +1.44 to 1.70 V (vs. NHE), depending on solvent, pH, etc. -very powerful oxidizing agent (cf. $O_2 + 4H^+ + 4e^- = 2H_2O$ [E_o = +1.23 V]; but Ce(IV) kinetically stable in H_2O).

Benzylic oxidation:



CAN : Ceric Ammonium Nitrate , $(NH_4)_2Ce(NO_3)_6$

Ln(III) as Lewis Acid Catalysts

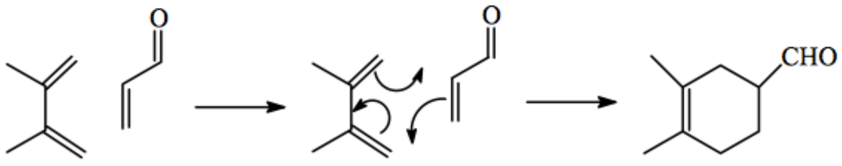
- All Ln^{3+} are large cations with +3 charge ⇒ Lewis acidity is moderate-high – useful in organic synth.

- Lanthanide contraction - monotonic **decrease** in ionic radius of Ln^{3+} across series ⇒ gradual **increase** in Lewis acidity across series. Possible to tune reactivity of catalyst systems by selecting appropriate Ln.

Anhydrous $Ln(O_3SCF_3)$, most frequently used Lewis acid (weakly coordinating OTf anion). Can be used in water or organic solvents

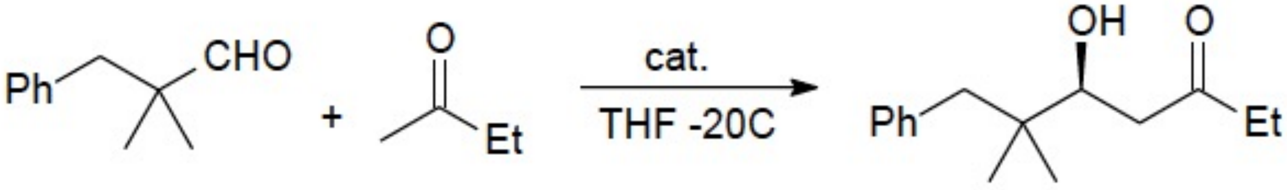
Also tris-diketonate complexes ($Ln(fod)_3$, fod = fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane- 3,5-dionato)

- Typical reactions catalysed by Ln3+:



- Diels-Alder and Hetero-Diels-Alder reaction
- Aldol reactions.
- Michael additions.
- Friedel-Crafts Reaction

Chiral Aryloxide Catalysts

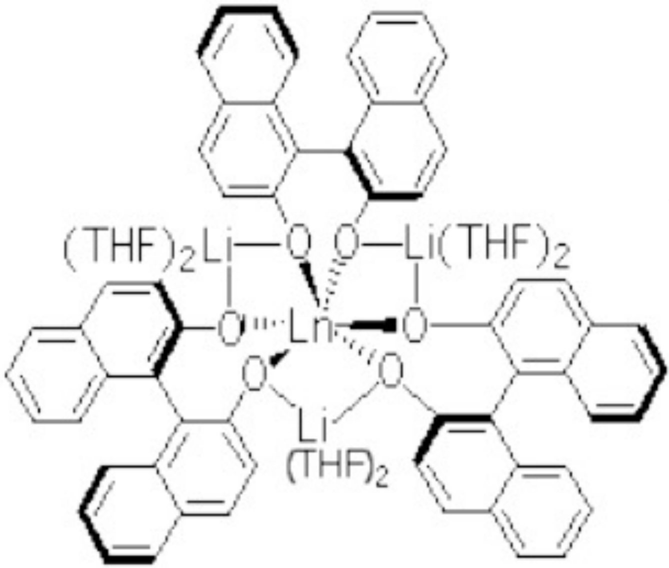


94%, *ee* = 71%

Enantioselective
Reduction of aldhehydes
(aldol reaction)
Also enantioselective
Diels-Alder reaction

Catalyst = (*R*)-La(BINOL)$_3$Li$_3$(THF)$_6$:

Soluble in ether or THF



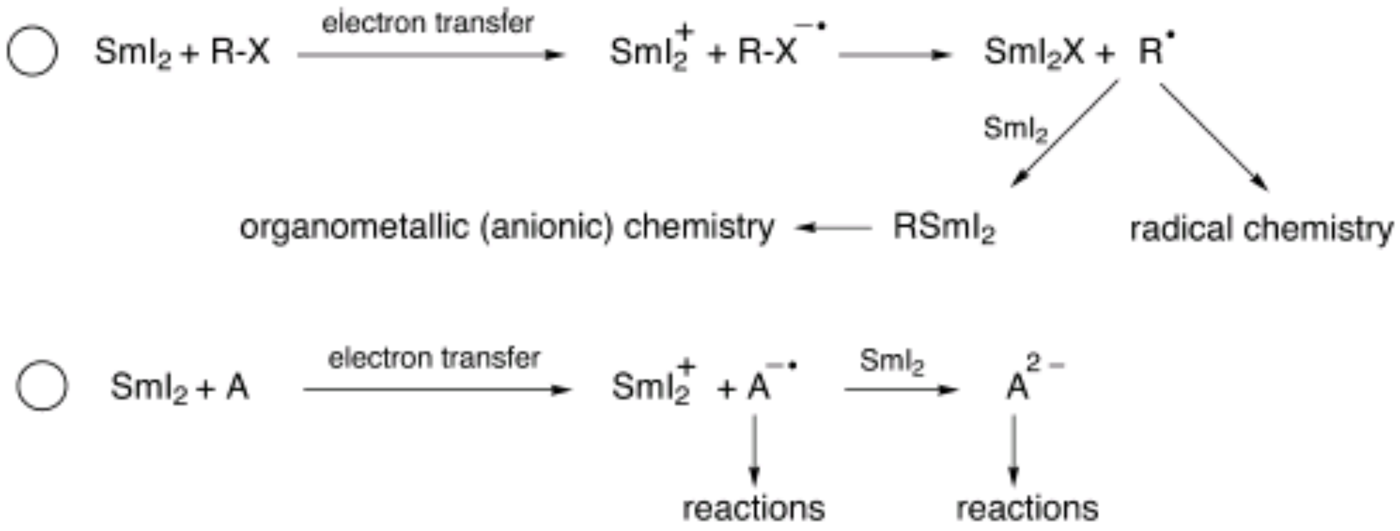
The cation is important
(cooperative substrate binding)
Addition of cryptand reduces ee

Chiral Lewis acid catalyst

[M. Shibasaki, N. Yoshikawa, *Chem. Rev.* **2002**, *102*, 2187]

Sm(II) in Organic Chemistry and Catalysis

Redox properties of SmI_2 ideal for mediating a variety of reactions involving one electron reduction of substrates (eg halogen compounds, ketones)

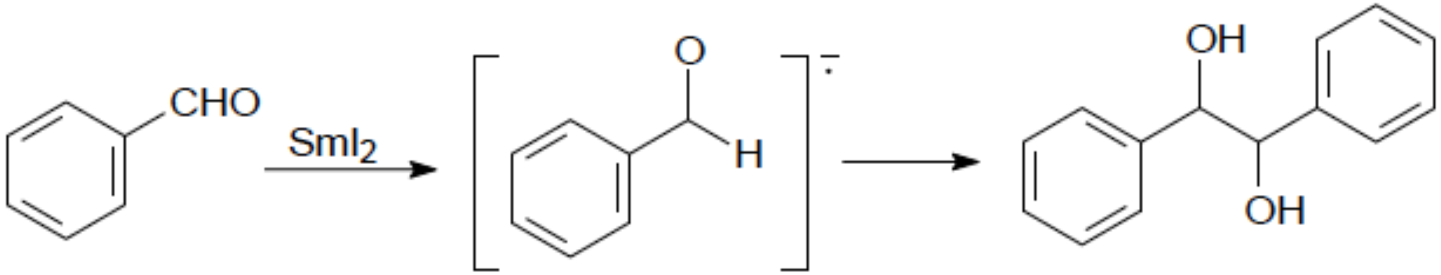


- Additives (transition metal catalysts and strong donor ligands) and solvents affect redox potential and/or accelerate reaction .
- SmI_2 reactions often very functional group tolerant.
- Frequently stereoselective (chelation control).

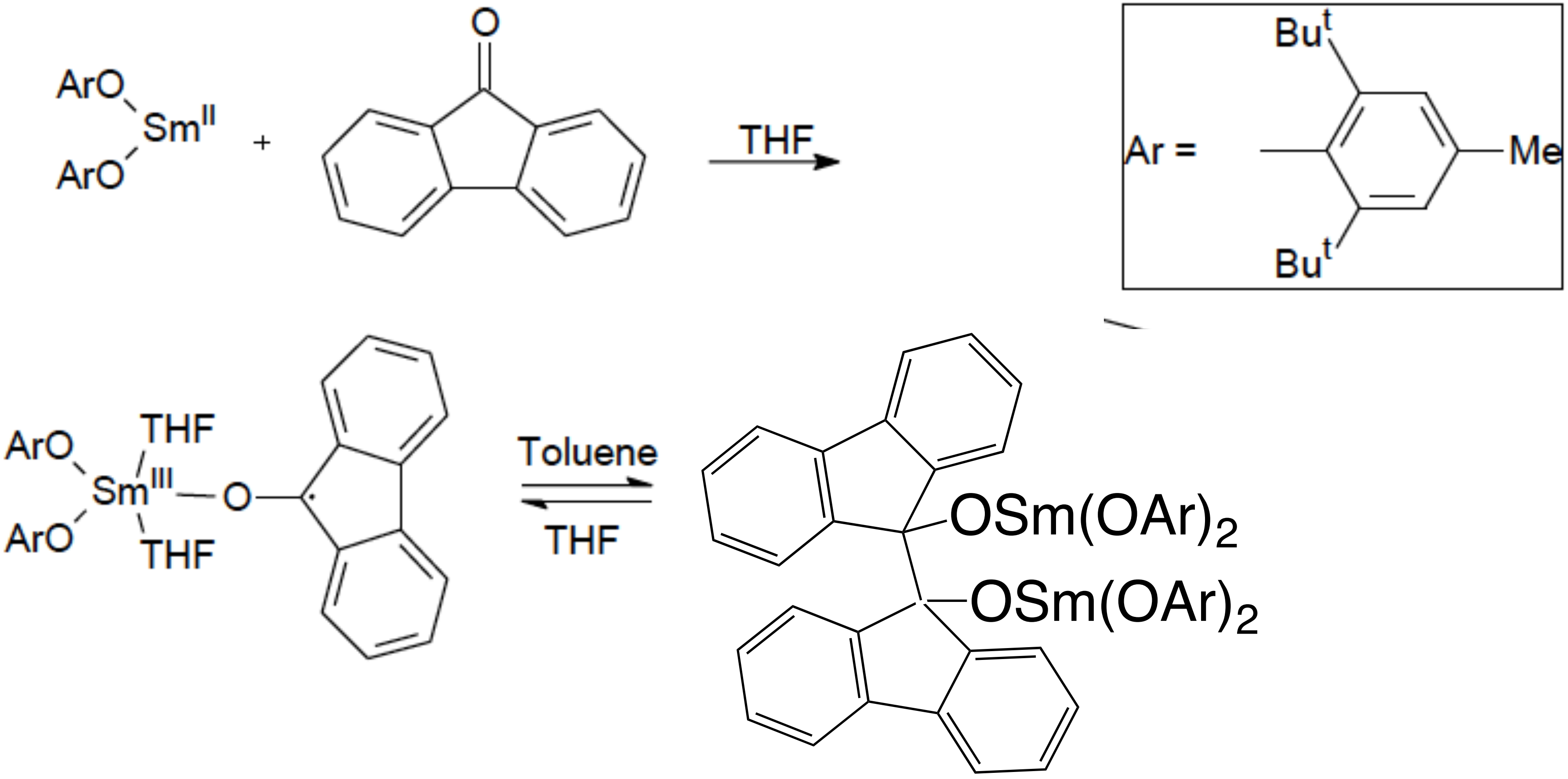
- Typical reactions:

- Alkyl radical-olefin couplings
- -Barbier-type reactions (addition of halogenoalkane to a carbonyl compound)
- Pinacol couplings

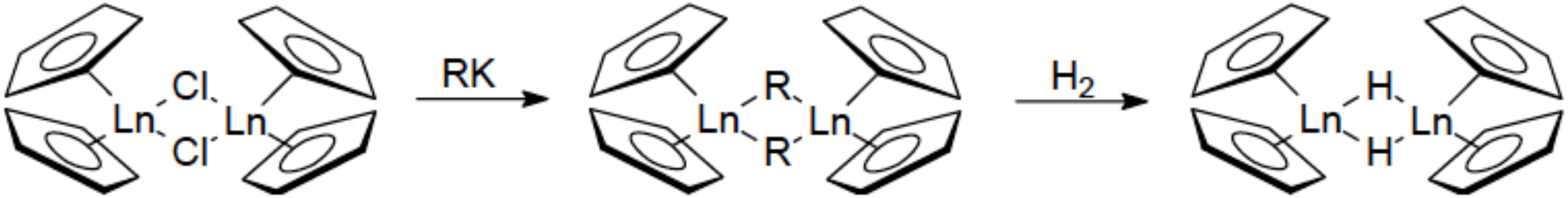
Pinacol Coupling Reactions



Radical intermediate can be isolated:



Ln^{3+} Organometallics in Catalysis



Cp_2LnH and Cp_2LnR (Cp = Cp*, $C_5H_3(SiMe_3)_2$, etc.) catalyse alkene transformations including:

- Hydrogenation
- Hydroamination
- Hydrosilylation
- Hydroboration
- Hydrophosphination
- Hydroalkoxylation
- Polymerisation

Ln^{3+} Catalysed Hydrogenation

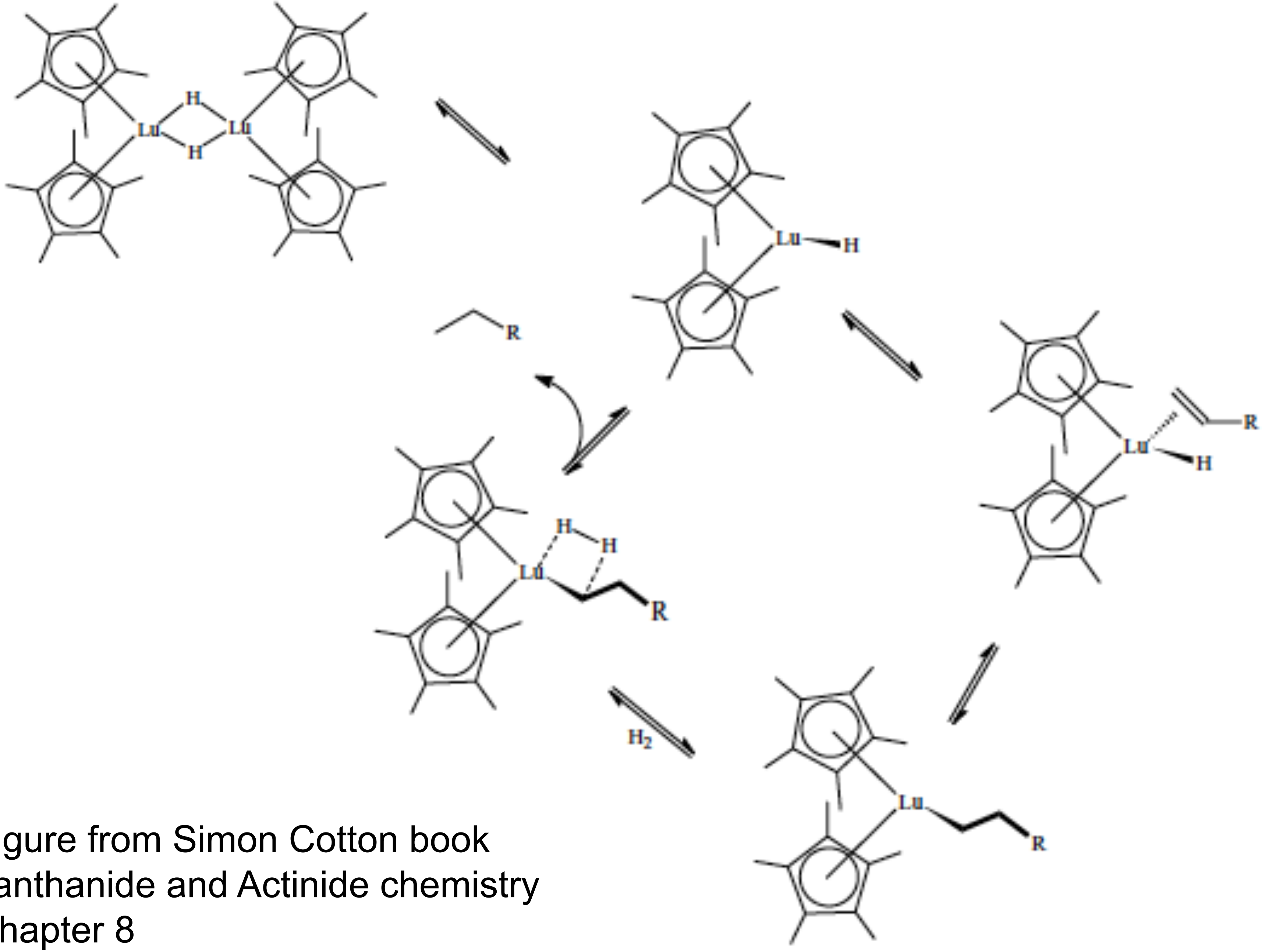


Figure from Simon Cotton book
Lanthanide and Actinide chemistry
Chapter 8

Hydroamination Catalysed by [Cp*$_2$La(CH(SiMe$_3$)$_2$)].

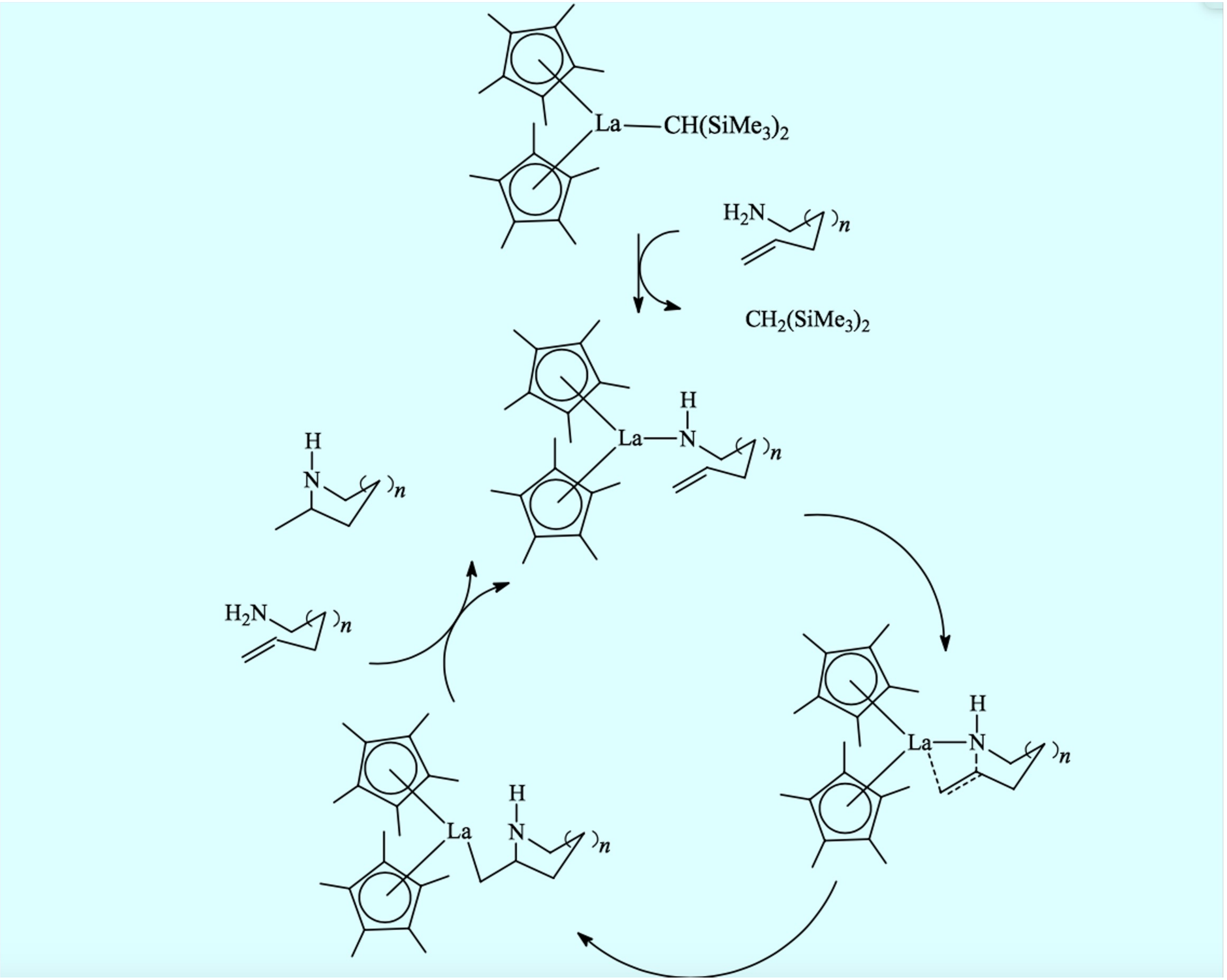


Figure from Simon Cotton book
Lanthanide and Actinide chemistry
Chapter 8

Actinides in Catalysis

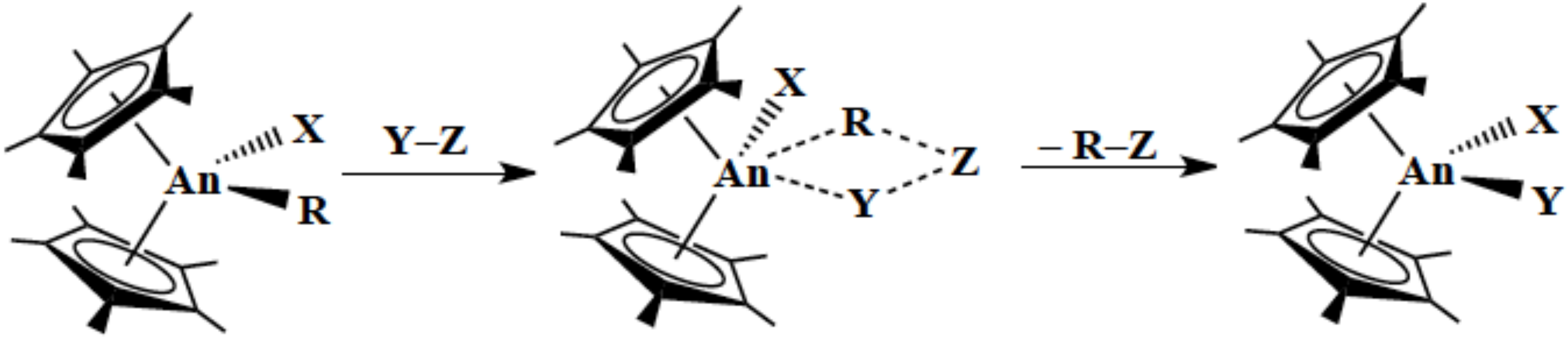
- Metals are highly electrophilic as expected for highly charged electropositive ions, like lanthanides and early transition metals

Reactions with oxygen containing substrates are most commonly stoichiometric not catalytic. The strength of the An-O bond can drive unusual reactions, but once formed, the An-O bond is so strong that it is not readily broken to generate a catalytic cycle.

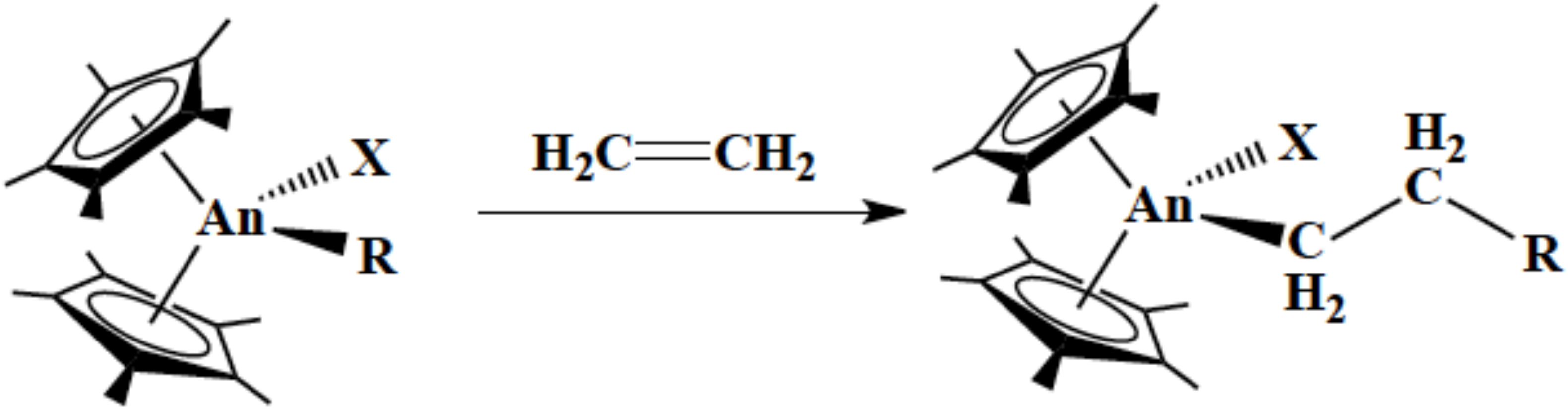
Catalysis is easier to achieve with heteroatom-free hydrocarbons. If an oxygen-containing substrate is involved, the cycle must trade a strong An-O for another strong An-O.

Main Processes in An(IV) Catalysis

Sigma-bond metathesis



Olefin insertion:



Marks, T. J. Dalton Transactions 2010, 39, 6576

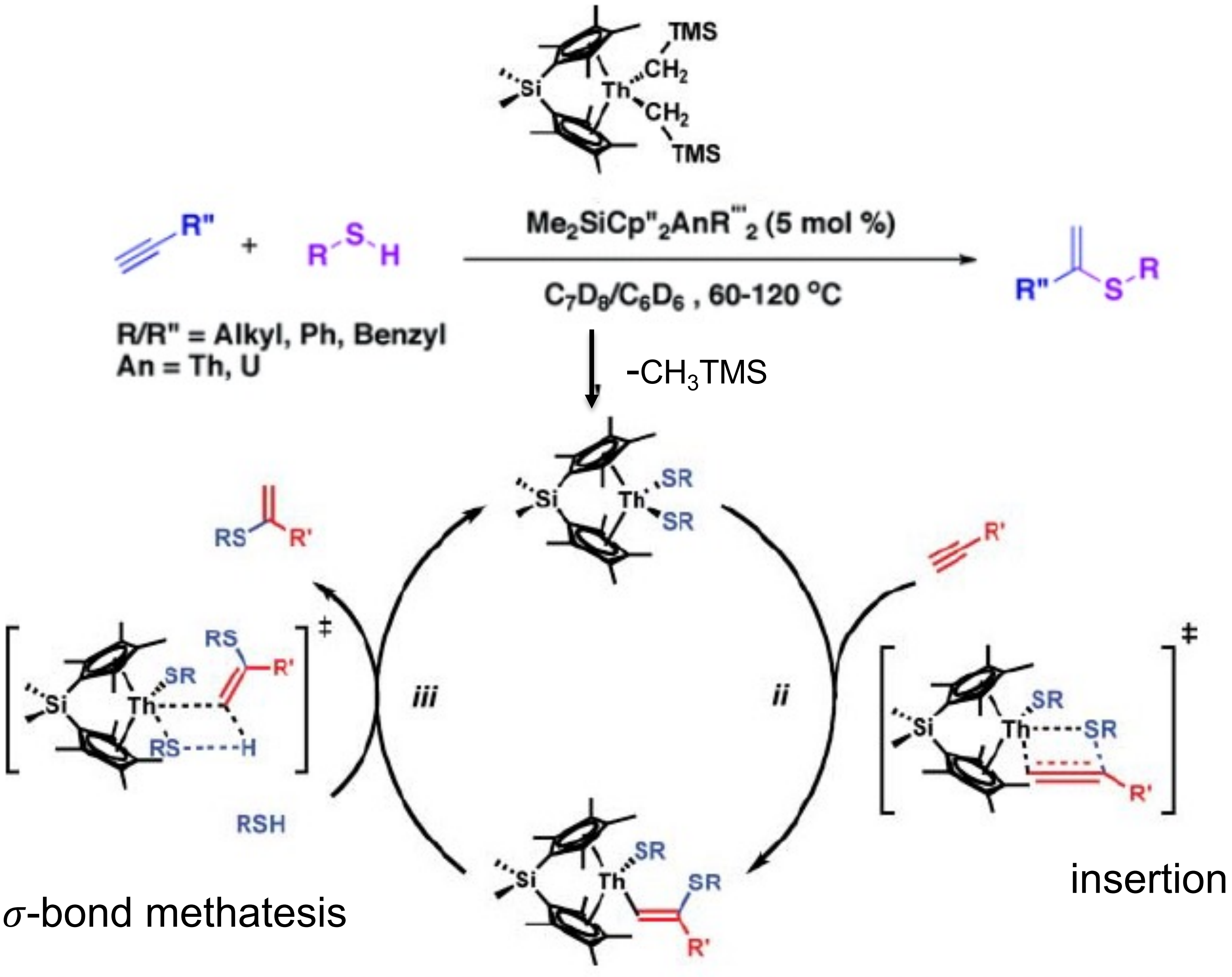
Actinides in Catalysis

There are no actinide based catalysts reagents commonly found in organic laboratories or in industry.
Nuclear applications more important for actinides than catalysis, but some examples of catalysis exists:

For example Actinide metallocenes, e.g. **$(C_5Me_5)_2UMe_2$**, can initiate all the "hydro" reactions such as hydrogenation,hydroamination,hydrosilylation,hydroboration Hydrophosphination, hydroalkoxylation, and hydrothiolation

Called hydroelementation or hydrofunctionalization by
Marks, T. J. Dalton Transactions 2010, 39, 6576

Actinide-Mediated Hydrothiolation of Terminal Alkynes



-CH$_3$TMS

insertion

σ-bond methatesis

Marks, T. J. J. Am. Chem. Soc., 2009,131, 2062.

Catalytic Synthesis of Ammonia
Fritz Haber

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3$$

Very important process in the production of fertilizers

To reduce nitrogen to ammonia high temperature and pressure are needed.

(150–250 bar and between 400–500 ° C)

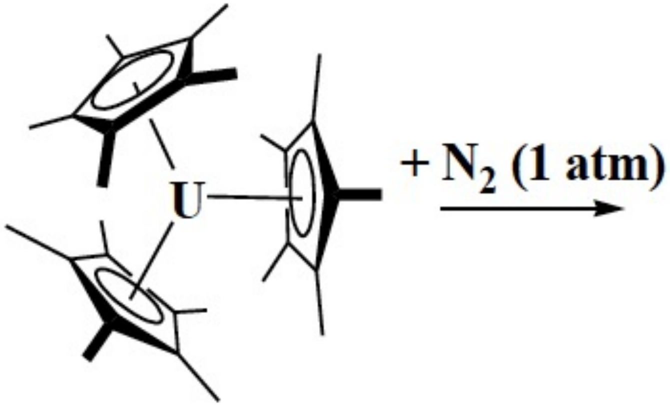
Haber examined many materials as catalysts.

Catalysts found early in the study in 1909 were osmium and uranium!

Uranium and uranium nitride more efficient catalysts but

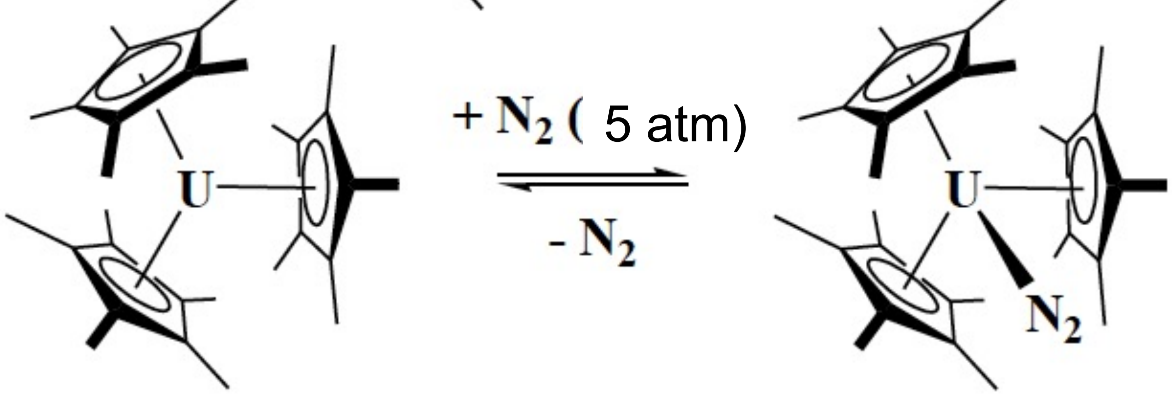
An iron based catalyst was developed by 1913.

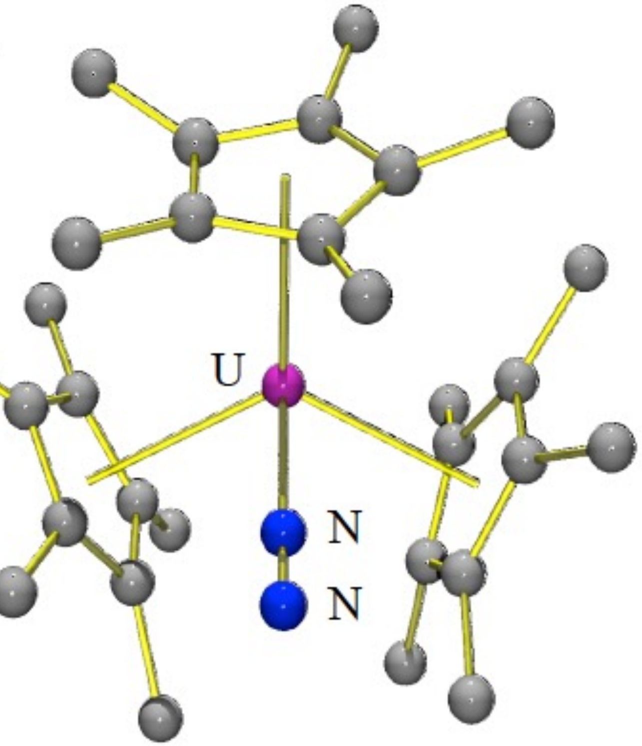
N_2 Binding in Molecular Systems



No reaction by ^{1}H NMR or FT-IR

5 atm required to crystallise
Not stable at 1 atm.

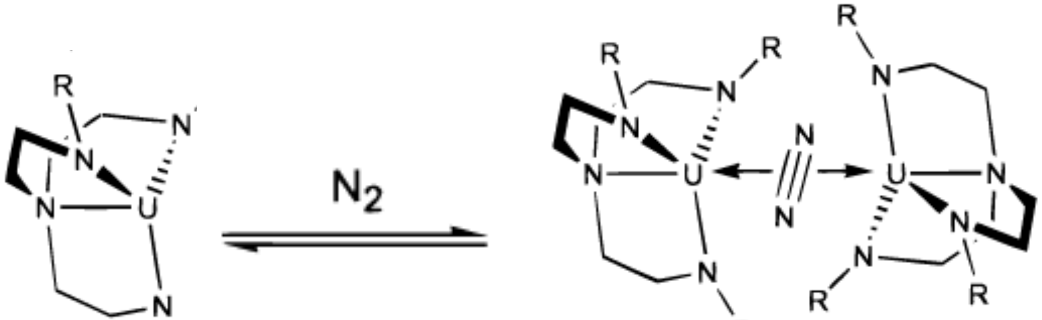




N≡N free 1.0975 Å

N-N	**1.120(14) Å**
ν(N_2)	**2207 cm^{-1} (KBr, IR)**
(Free N_2	**2331 cm^{-1})**

N_2 Binding in Molecular Systems



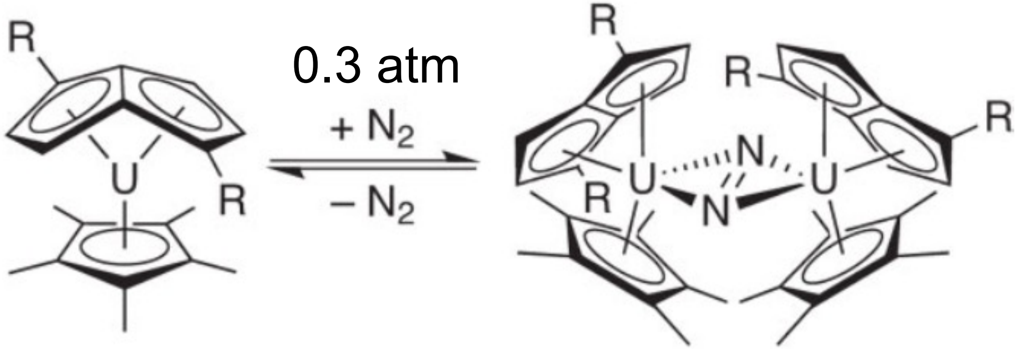
2U(III) and N_2

Scott, 1998
Reversible N_2 binding
Stable at 1 atm,
reversible in vacuo
N≡N 1.109(7) Å
No activation

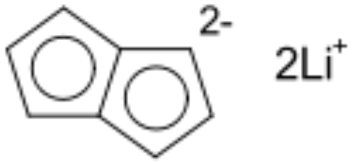
R= ${}^{t}BuMe_2Si$

R= ${}^{i}Pr_3Si$

Cp/pentalenide
U(III) complex



2U(IV) and N_2^{2-}

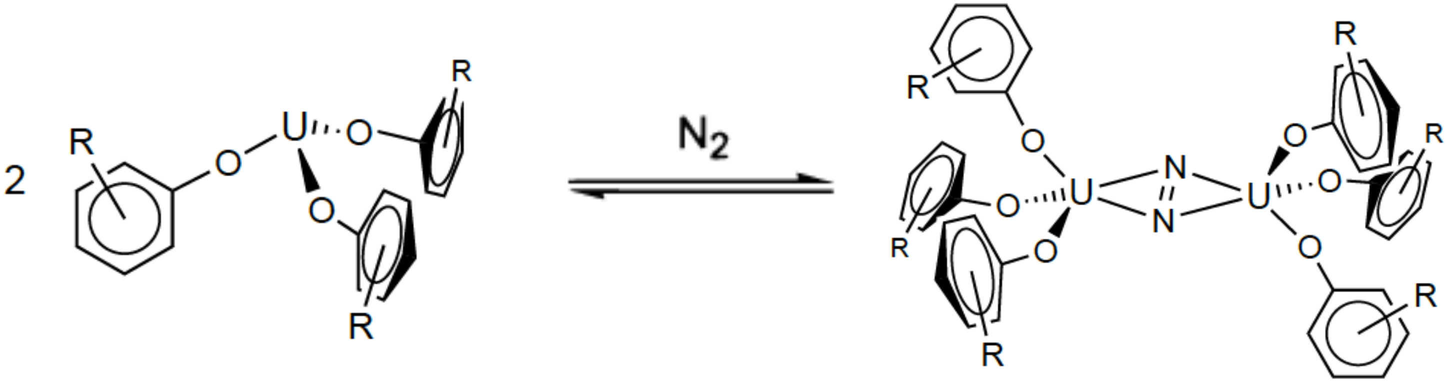


pentalenide

N≡N free 1.0975 Å

N=N 1.232(10) Å
Activation !
N_2 dissociates in vacuo
And solution

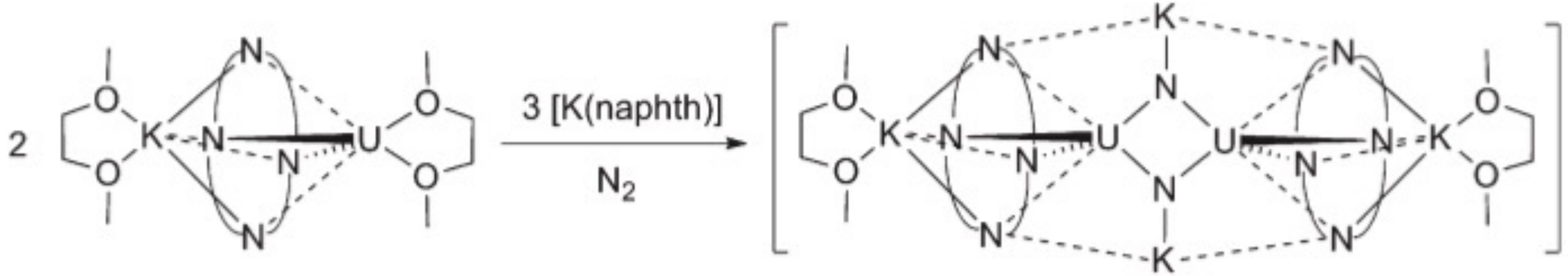
N=N 1.163(19) –
1.236(5) Å
Activation !



2U(IV) and N_2^{2-}

N_2 Reduction in Molecular Systems

One example!



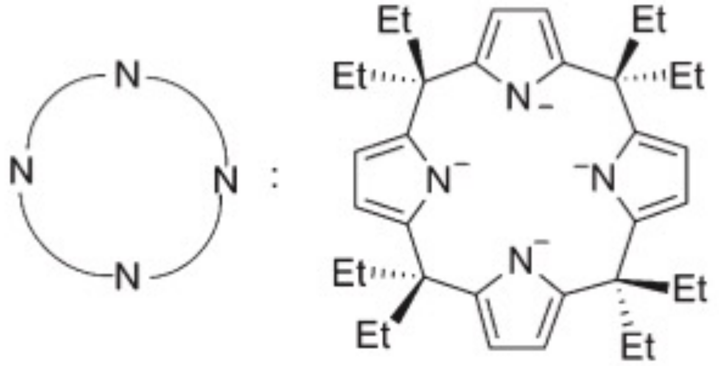
16

U(III)

17

U(V)/U(IV)

[K(dme)$_4$]



$N_2 \xrightarrow{6\ e^-} 2\ N^{3-}$

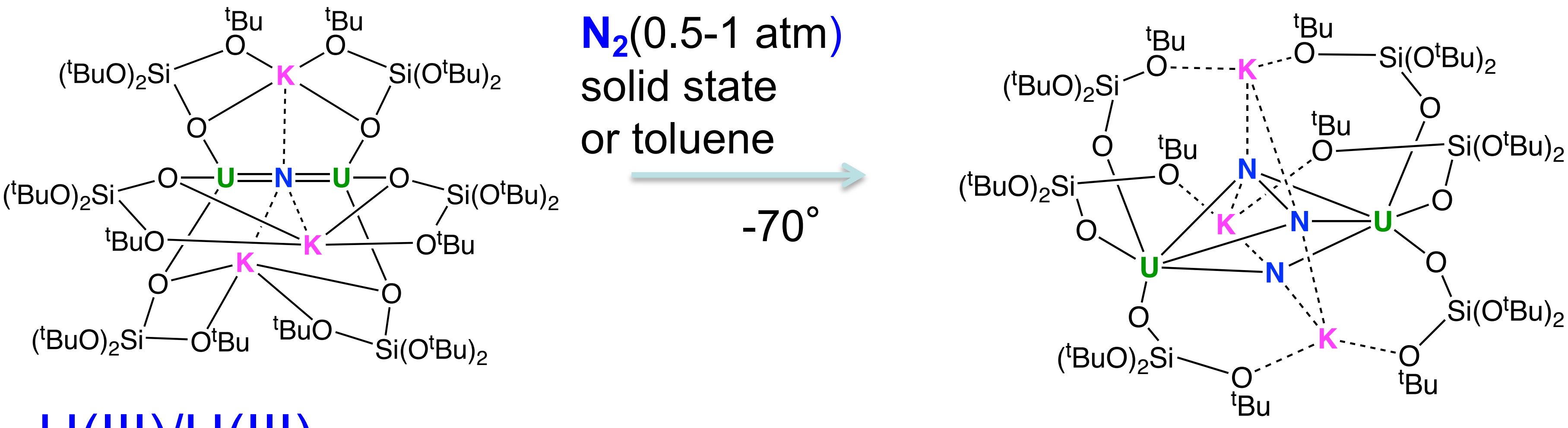
$U(III) \xrightarrow{-\ 2\ e^-} U(V)$

$U(III) \xrightarrow{-\ 1\ e^-} U(IV)$

$3\ K \xrightarrow{-\ 3\ e^-} 3\ K^+$

U(II) intermediate??
Importance of a cooperative binding by K

N_2 Reduction by Nitride Bridged U(III) Complexes



N_2(0.5-1 atm)
solid state
or toluene

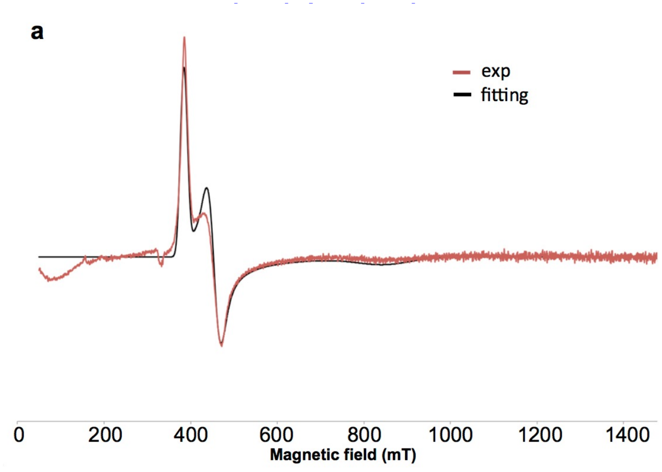
-70°

U(III)/U(III)

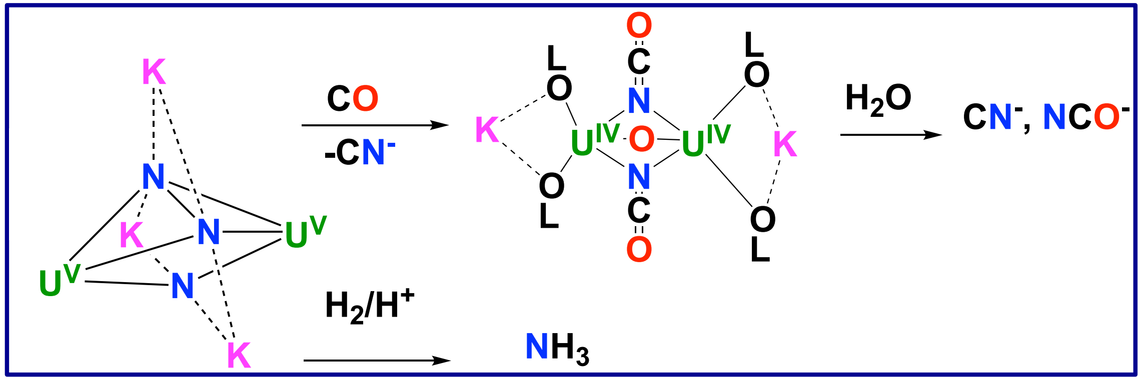
N-N:1.521(18) Å

68%

U(V)/U(V)-N_2^{4-}

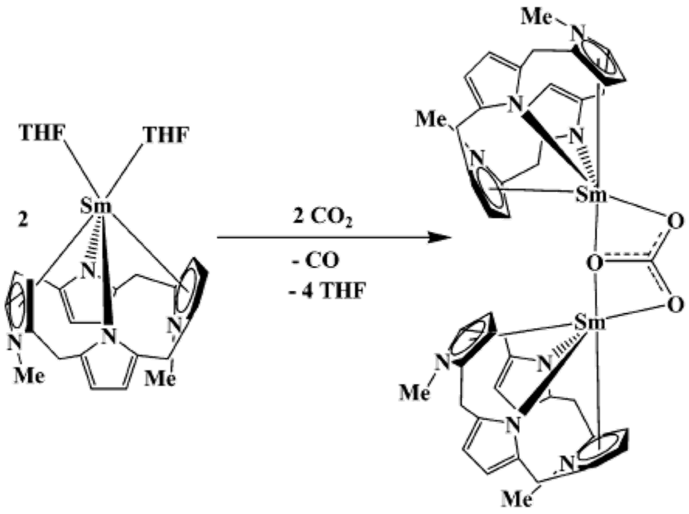


μ_{eff} per U= 1.80 μ_B



Falcone et al Nature, **2017**, 547, 332-335

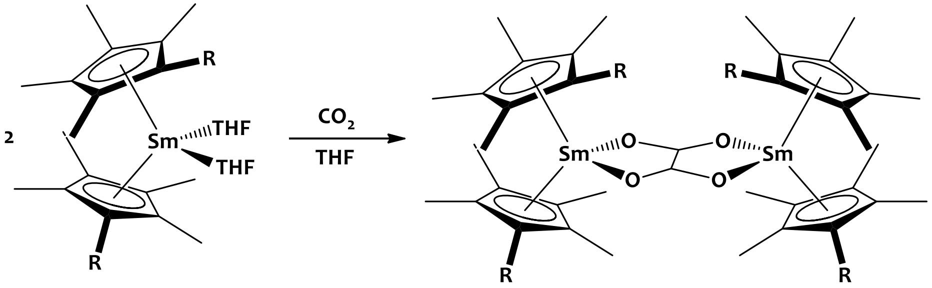
CO_2 Reduction in Sm(II) Systems



Disproportionation of CO_2:

$$\underbrace{2\,CO_2 + 2\,e^-}_{CO_2^{\cdot -}} \rightarrow CO_3^{2-} + CO$$

M. G. Gardiner *et al.*, *Chemm. Commun.*, **2006**, 16, 4853-4855

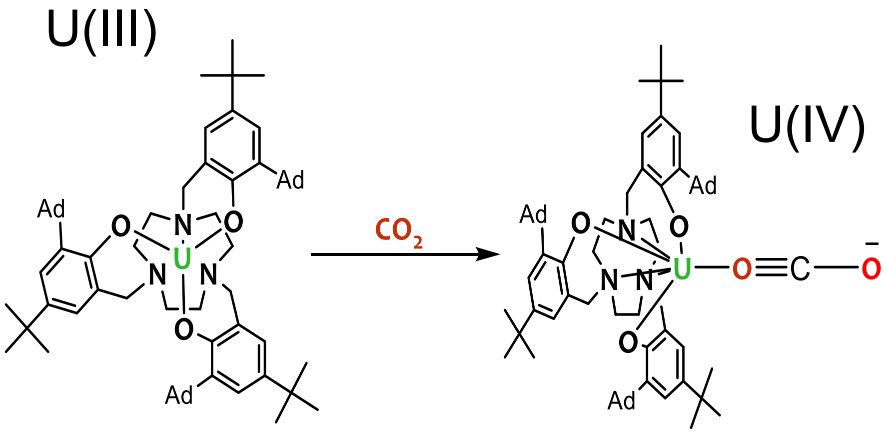


Reductive coupling of CO_2:

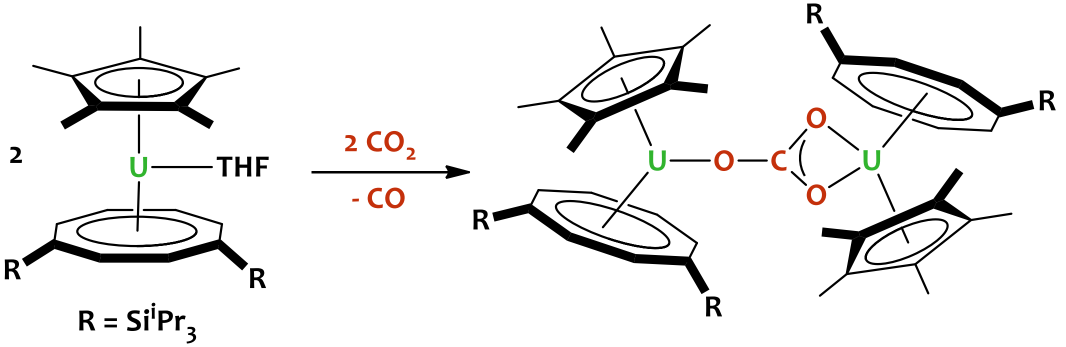
$$\underbrace{2\,CO_2 + 2\,e^-}_{CO_2^{\cdot -}} \rightarrow C_2O_4^{2-}$$

W. Evans Inorg.chem 1998

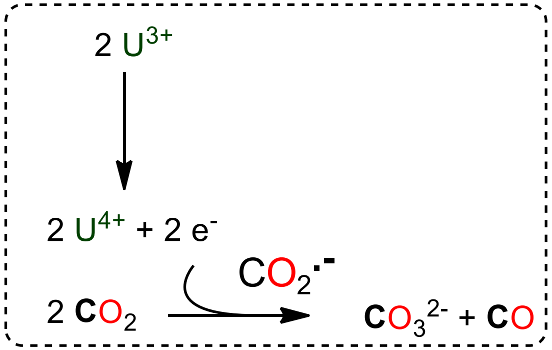
CO_2 Reduction in U(III) Systems



One e⁻ CO_2 reduction K. Meyer 2004



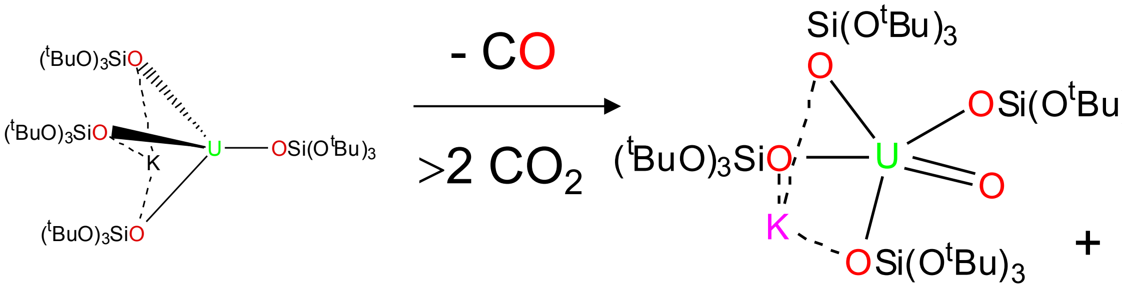
CO_2 reductive disproportionation Cloke 2009



$2\ U^{3+}$

$2\ U^{4+} + 2\ e^-$

$2\ CO_2 \xrightarrow{CO_2^{\bullet -}} CO_3^{2-} + CO$



U(III)

U(V)

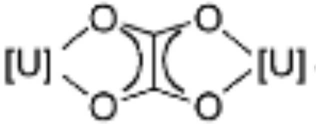
Remarkable 2e⁻ oxidation of uranium with carbon dioxide.

Reductive deoxygenation

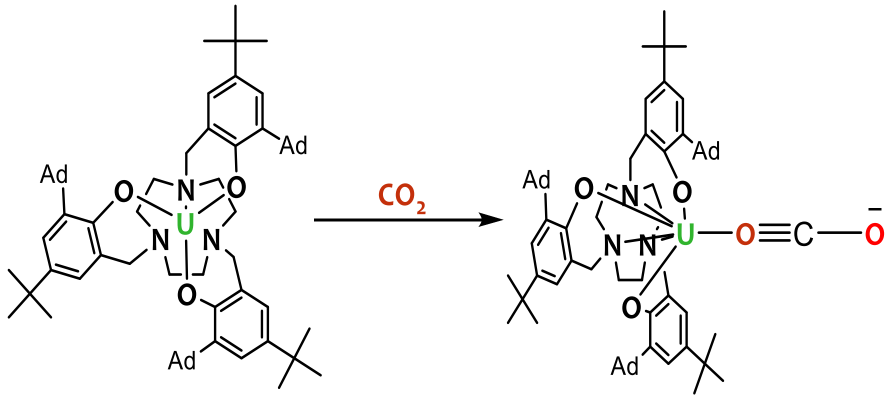
Two electron transfer by two U(III)

CO_2 reductive coupling to oxalate Cloke 2014

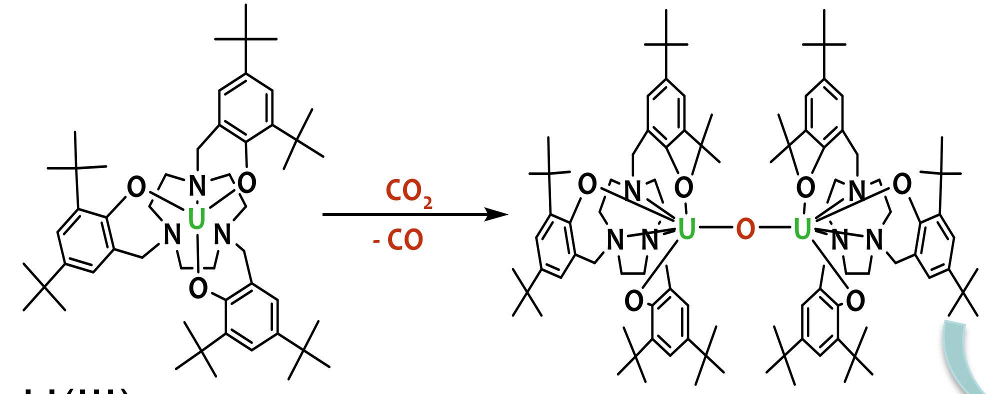
Also occurs depending on steric bulk of R on Cp



CO_2 Reduction in U(III) Systems



The nature of substituents
Changes the reduction product

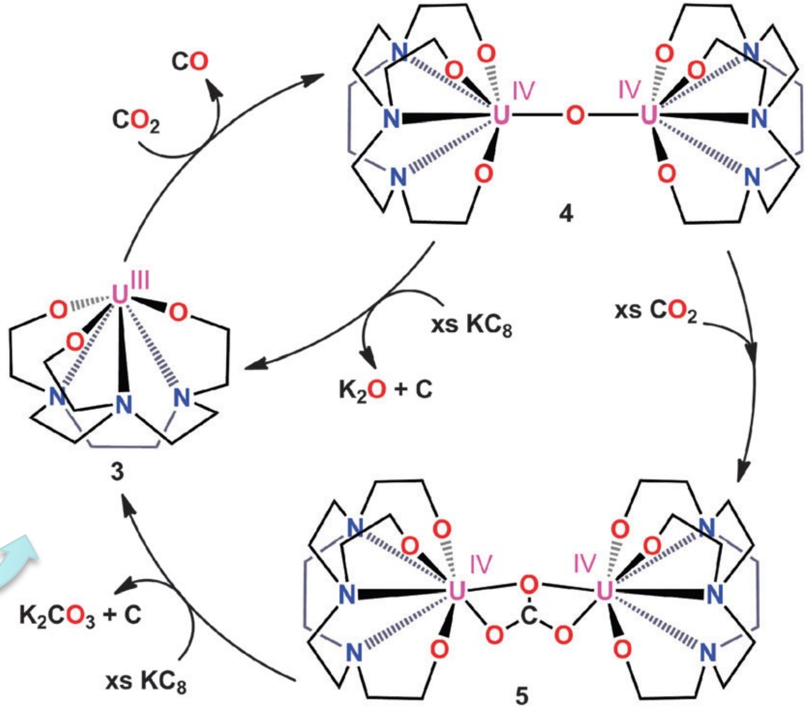


U(III)

2 U(IV)

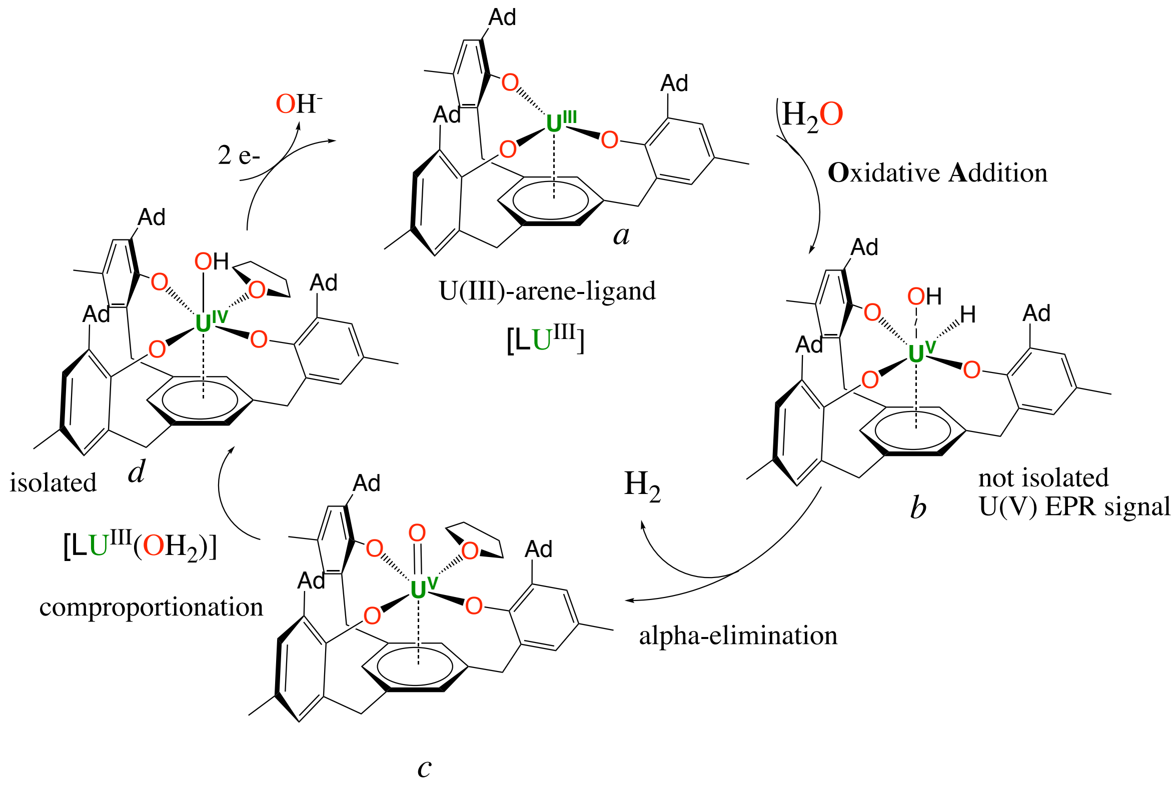
Reductive deoxygenation

Synthetic Cycle

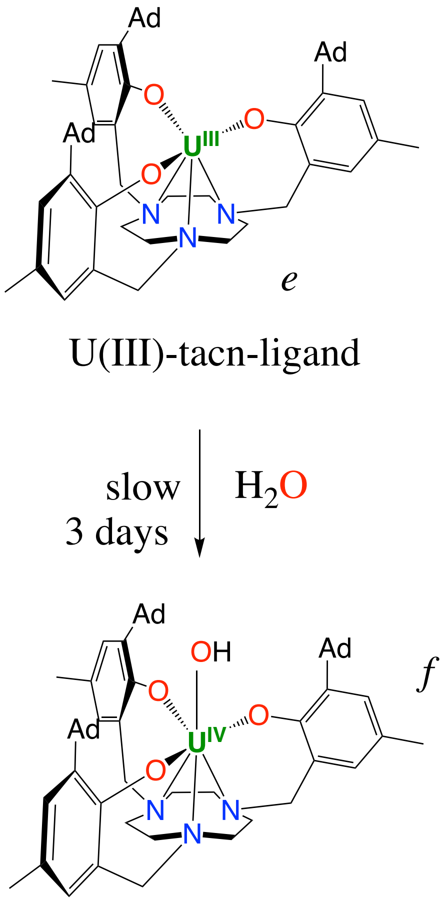


A Uranium Electrocatalyst for Water Reduction

Water Reduction Catalyst!



Not a catalyst!



U(III) acts as an electrocatalyst
Reduces overpotential of 0.5 V
Yield and turnover comparable to best
Transition metal catalysts

Important role of the ligand

Meyer, Nature 2015, 317, Nature Chemistry 2018, 259
Nature Chemistry 2018, 247

On the exam day you need a periodic table
and a calculator but NO phones and
NO access to internet is allowed

You can also bring a one side A4 page
with your notes