Coordination Chemistry and Reactivity of f Elements

Cours 7: Organometallic Chemistry

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Learning Objectives

-Know why these complexes are very unstable to water and oxygen

-Know that the bonding has a very polar character

-Identify possible synthetic routes to the different species

-Know some examples of reactivity

Know that organo-An chemistry is,
more diverse than organo-Ln chemistry (Th, U, Np, PU rich redox chemistry)

Know that oxidative addition and reductive elimination are accessible to An

Remember examples of organospecies in different oxidation states

Know what a delta bond is

M–C bonds in the f-Block

- Fundamental research

- Homogeneous catalysis small-molecule activation

- CVD applications (MOCVD:
metal-organic chemical vapour deposition)

Organo-lanthanide chemistry:
All Ln in the +3 oxidation state well known in the +2 oxidation state – Sm, Eu, Yb (limited for others)

Organo-actinide chemistry
Known in oxidation state: +3, +4, +5, +6 (limited +2 chemistry)
varying trends in oxidation state stability

M–C stability in the f-Block

- f-Block ‘cations’ are hard acids, they form stable complexes with hard donors

- C-donor ligands are soft bases

f-block organometallics are thermodynamically very unstable with respect to aerial oxidation and hydrolysis:

stable complexes are formed under argon in rigorously dry non reactive organic solvents

Also very unstable to hydrolysis and oxidation are the hydride, amide, alkoxide, phosphide, thiolate complexes leading to hydroxide or oxides complexes

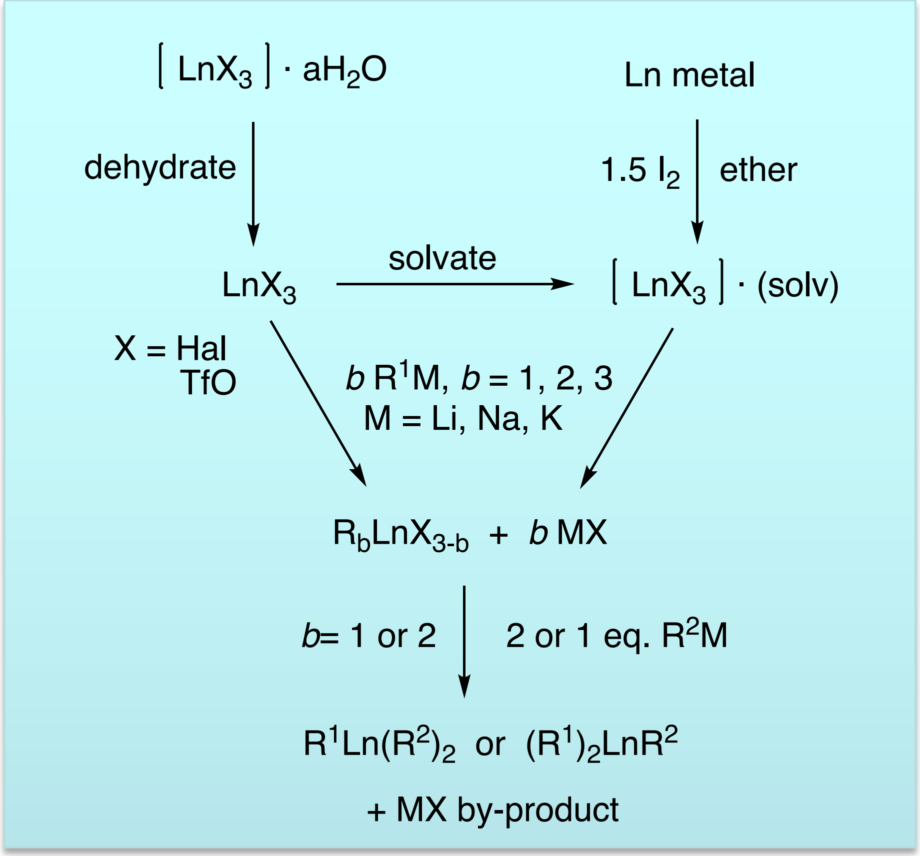
Handling organometallic compounds of f elements

Oxidation and hydrolysis can occur from non rigourous handling. Less stable than d-block organometallics

‘Adventitious’ H_2O
= wet solvent
= impure/wet commercial chemicals

‘Adventitious’ O_2
= poor quality ‘inert’ gas (N2 or Ar)
= loose connections

Synthesis of Ln organometallic compounds: Salt metathesis



$[LnX_3] \cdot aH_2O$

dehydrate

Ln metal

1.5 I_2 ether

LnX_3

solvate

$[LnX_3] \cdot (solv)$

X = Hal
TfO

b R^1M, *b* = 1, 2, 3
M = Li, Na, K

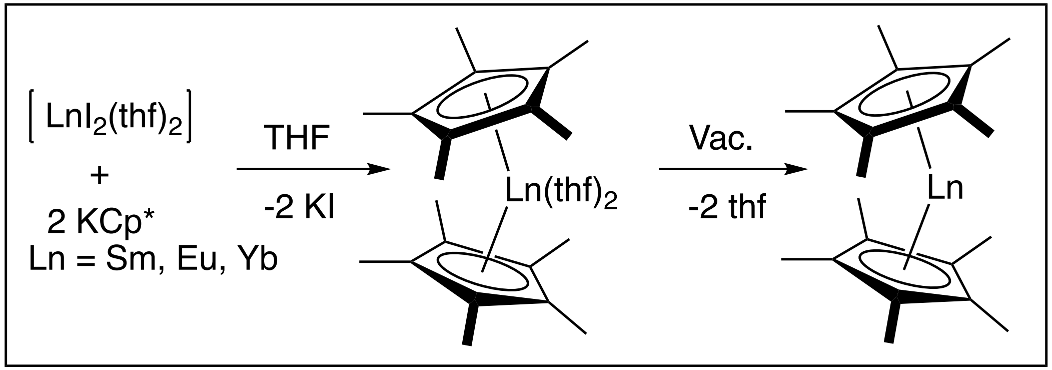
R_bLnX_{3-b} + *b* MX

b= 1 or 2

2 or 1 eq. R^2M

$R^1Ln(R^2)_2$ or $(R^1)_2LnR^2$

+ MX by-product



- Broad scope
- Driven by the formation of MX

- Unwanted « ate » complexes can form

R3Ln-C-----Li

- Stable solvate complexes can form

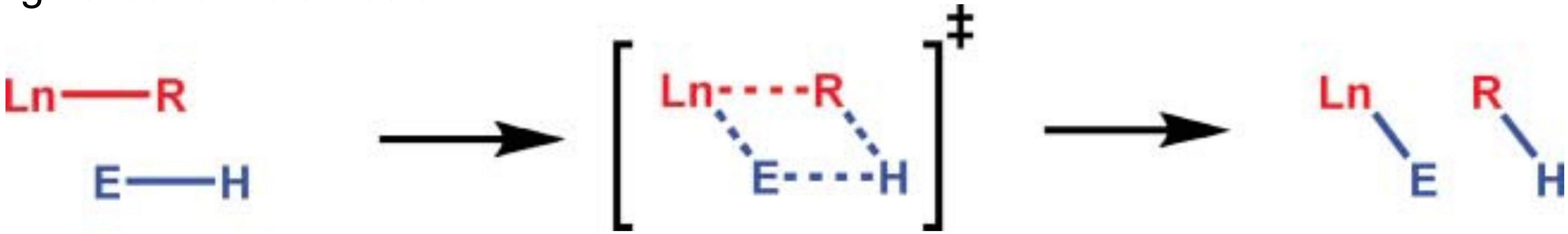
- Heteroleptic complexes can be prepared

-Both Ln(III) and Ln(II) can be prepared

Ln^{3+} Organometallics Reactivity

Ln^{3+} ions have high electrophilicity and kinetic lability; organolanthanide(III) compounds exhibit two major reaction patterns:

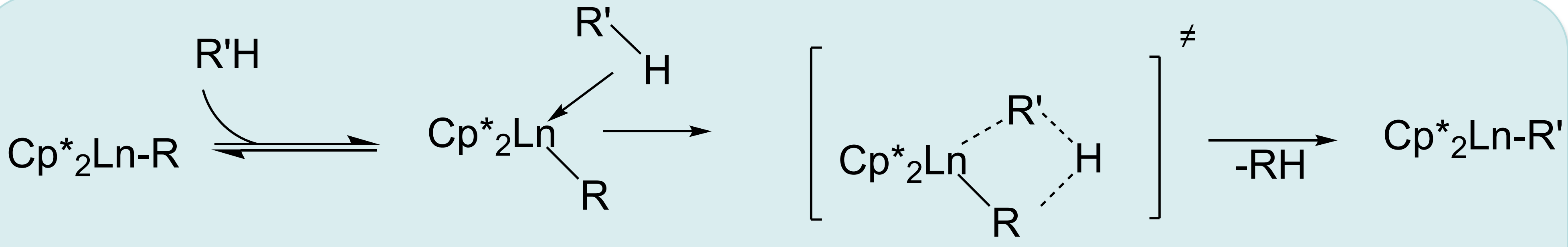
Sigma-bond metathesis



Olefin insertion:

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

Reactivity: σ-bond metathesis



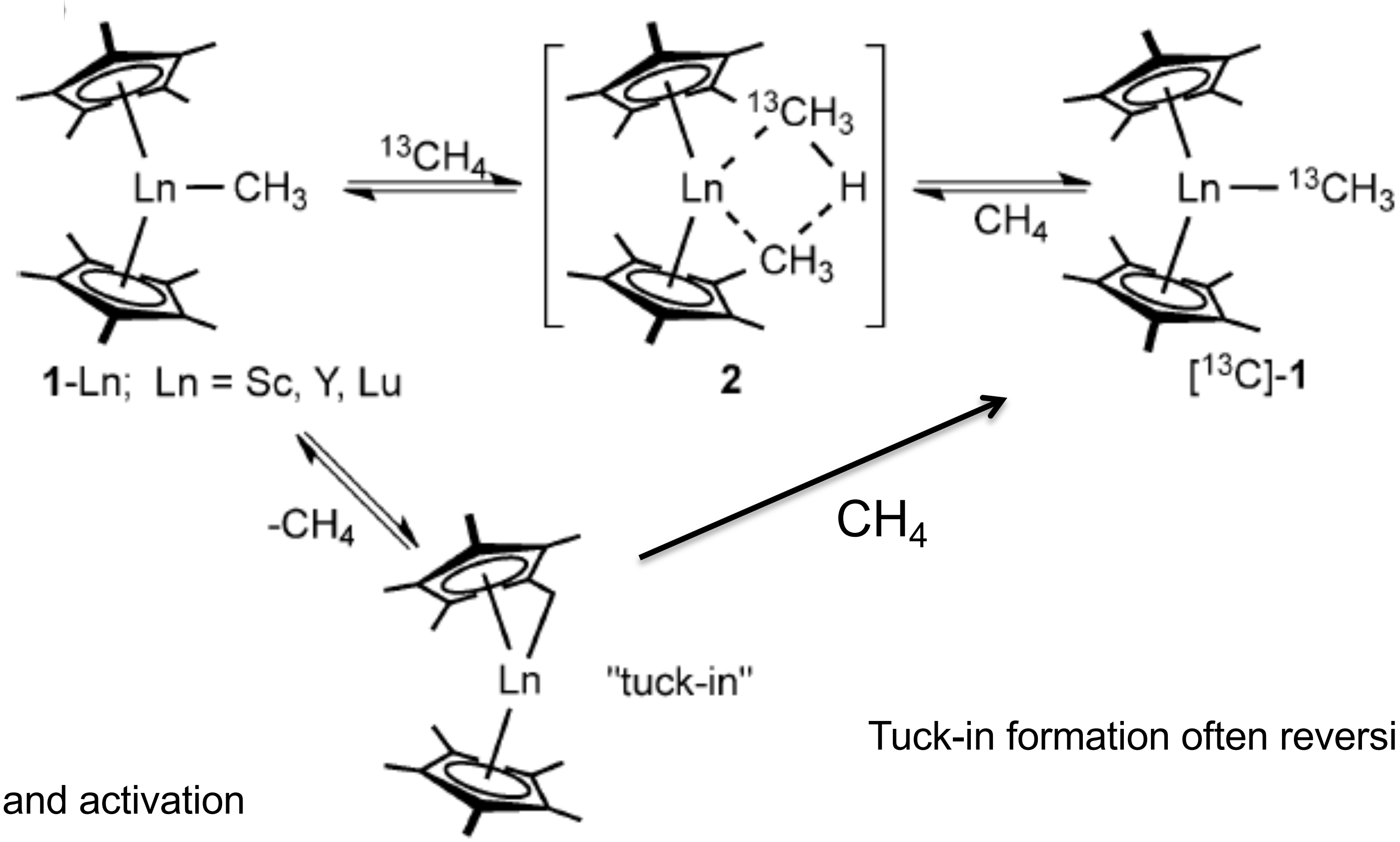
Concerted process that involves a 4-centred transition state

Impressive example of C–H activation of very unreactive substrates:

$$Cp^*_2Lu{-}CH_3 + {}^{13}CH_4 \xrightleftharpoons{70^\circ C} Cp^*_2Lu{-}{}^{13}CH_3 + CH_4$$

- Small radii of Sc^{3+} and Lu^{3+} thought to be important
- Ligand sterics play a role in determining reaction rate

C-H activation via σ-bond metathesis



1-Ln; Ln = Sc, Y, Lu

2

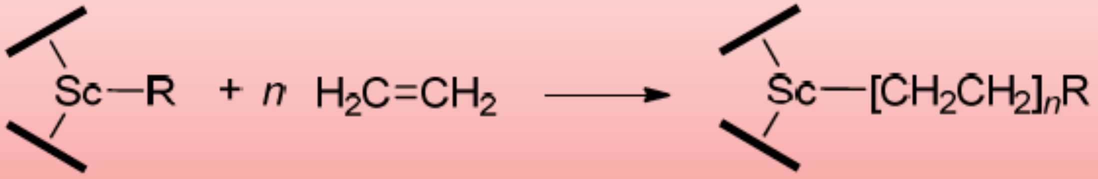
[^{13}C]-**1**

Tuck-in formation often reversible

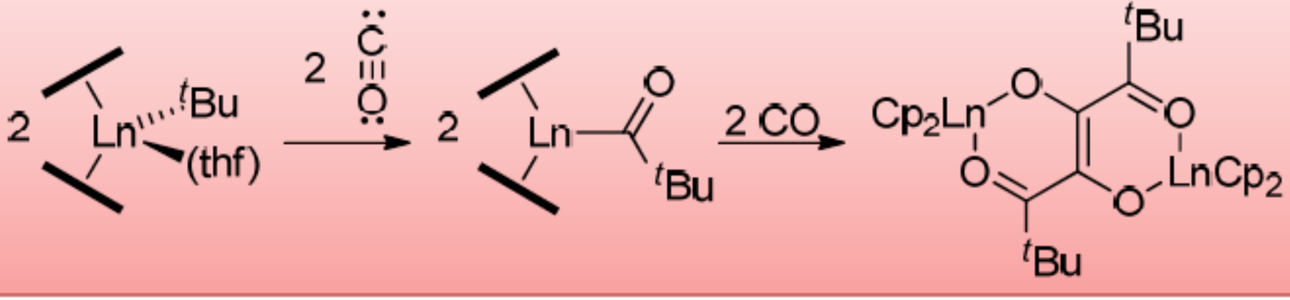
Possibility of ligand activation

Ln-alkyl bonds are polar: favor insertion reactions

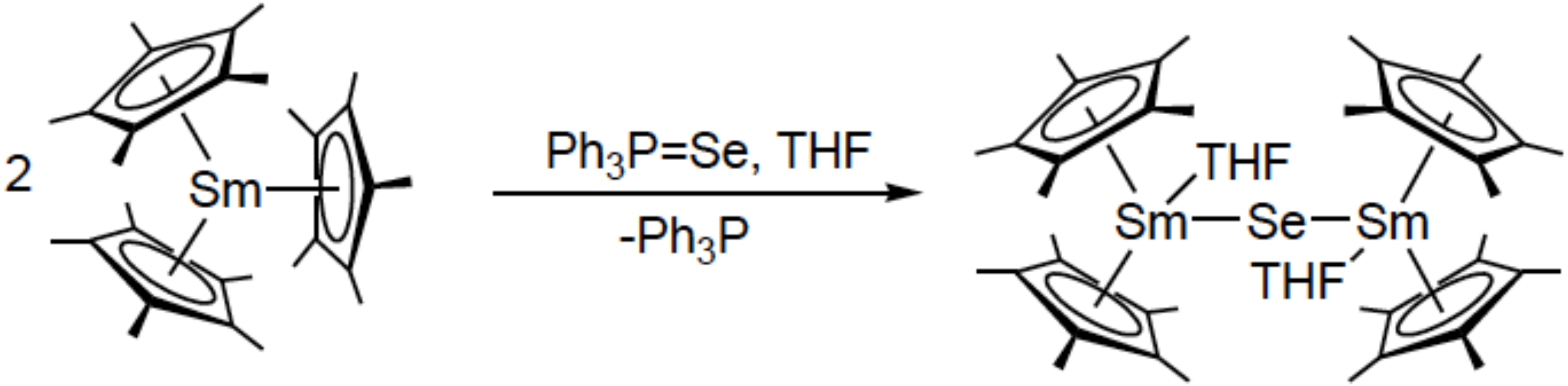
- Insertion polymerization (competes with σ-bond metathesis):



- CO insertions:

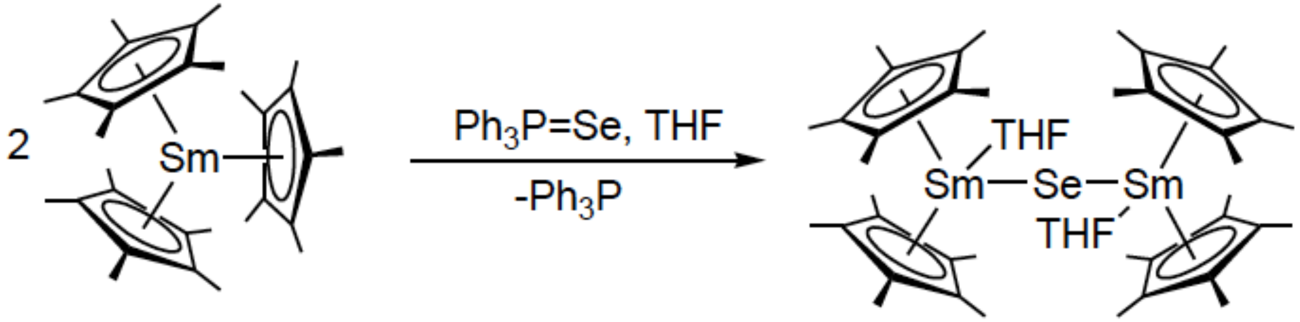


$LnCp^*_3$:Sterically-Induced Reduction (SIR)

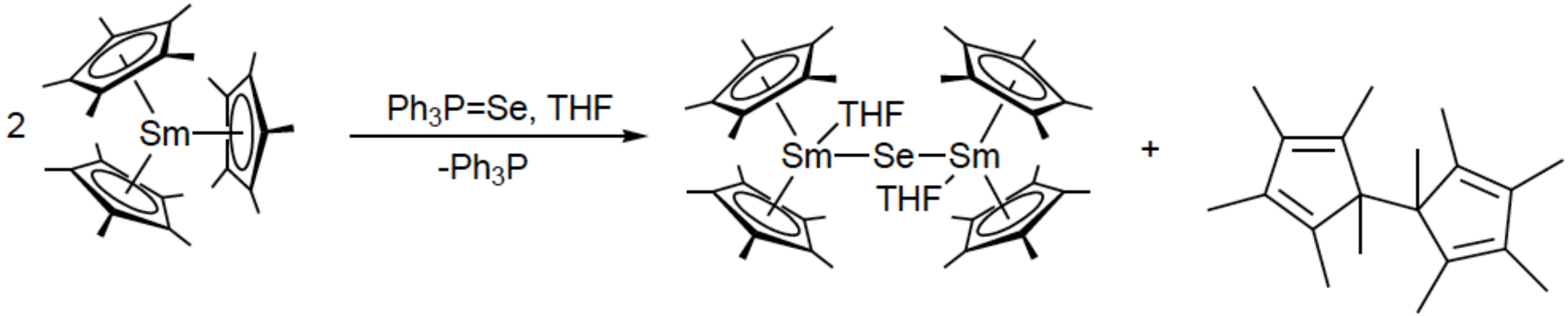


Sm(III) → Sm(III) - What is the reducing agent?

$LnCp^*_3$:Sterically-Induced Reduction (SIR)



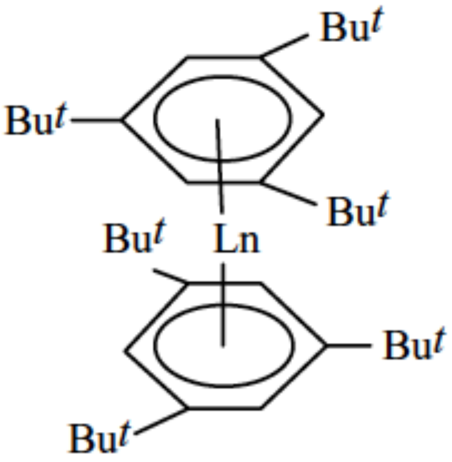
Sm(III) → Sm(III) - What is the reducing agent?



[Cp*]⁻ acts as 1-e reducing agent – Sterically-Induced Reduction (SIR).

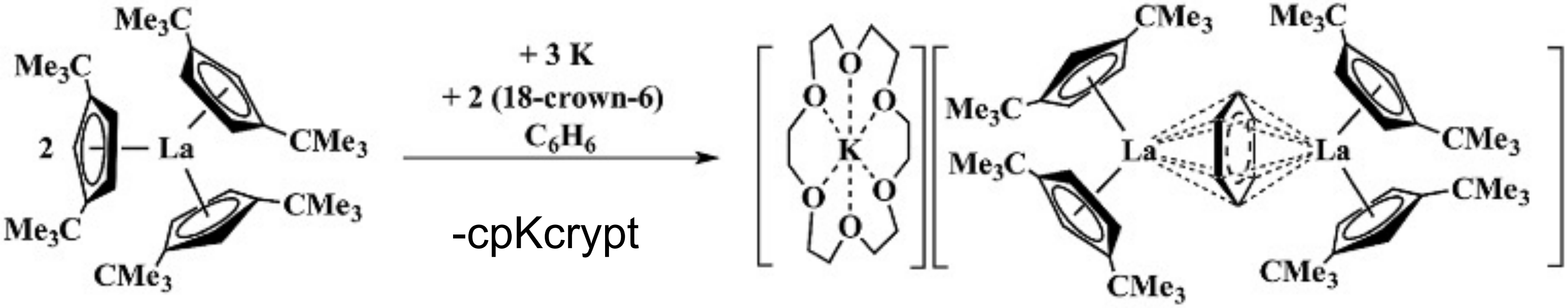
Lanthanide Arenes

Complexes of neutral π-acceptor ligand such as CO are not stable for Ln(0) :
arene an exception?



Prepared by co-condensation of vapourized lanthanide atoms with 1,3,5-tri-t-butylbenzene at 77 K

Ce, Eu, Tm, and Yb could not be isolated
May be related to possibility of promoting from f^ns^2 to $f^{n-1}s^2d^1$
Formally the Ln is in DO =0 but probably the DO is higher



Cp ’’ =1,3-$(SiMe3)_2C_5H_3$

With cp’’ reduction leads to
a La^{II}(tris-cp) complex

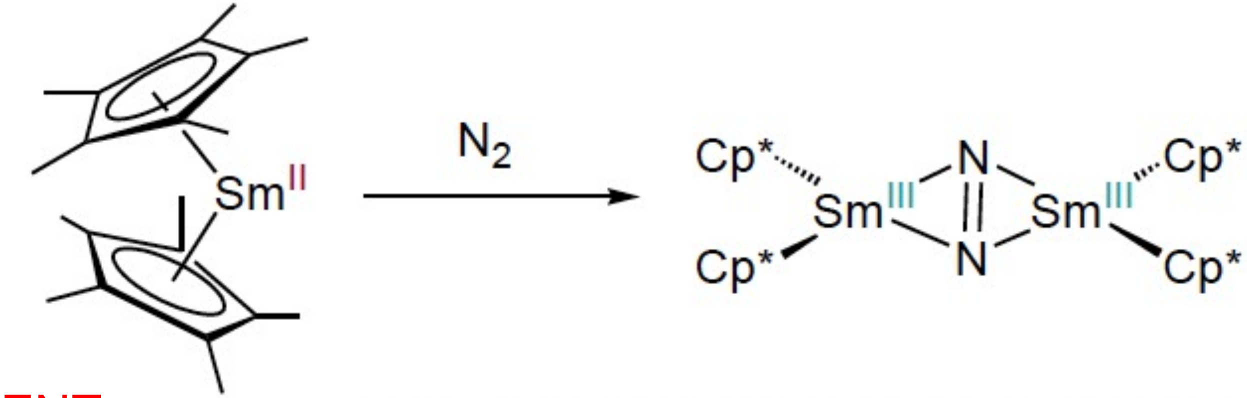
Possible electron configuration:
Ln(II) complexes of $(C_6H_6)^{-1}$
Ln(III)/Ln(II) complex of $(C_6H_6)^{-2}$

Lanthanide(II) cyclopentadienyl complexes

$$LnI_2(THF)_2 \quad + 2KCp^* \xrightarrow[-\,2\,KI]{} [LnCp^*_2(THF)_2] \xrightarrow[VACUO]{\Delta} [LnCp^*_2]$$

Ln =Sm, Eu, Yb

Redox couple (Sm^{II}/Sm^{III}) enhanced in Cp^*_2Sm vs. $SmI_2 \Rightarrow Cp^*_2Sm$ undergoes highly unusual reactions:



N_2 reduced to N_2^{2-}

[Cp^*_2Sm must be handled under Ar]

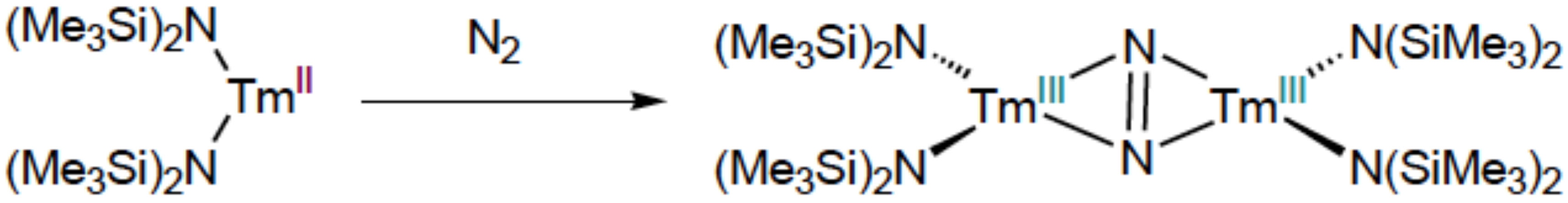
BENT metallocenes

[N.B. No reaction for $Cp^*_2Sm(THF)$]

Similar behaviour for "non-classical" $Cp^*_2Ln^{II}$ [Ln = Tm, Nd, Dy]

Reactivity: adduct formation with Lewis bases and one-electron reduction

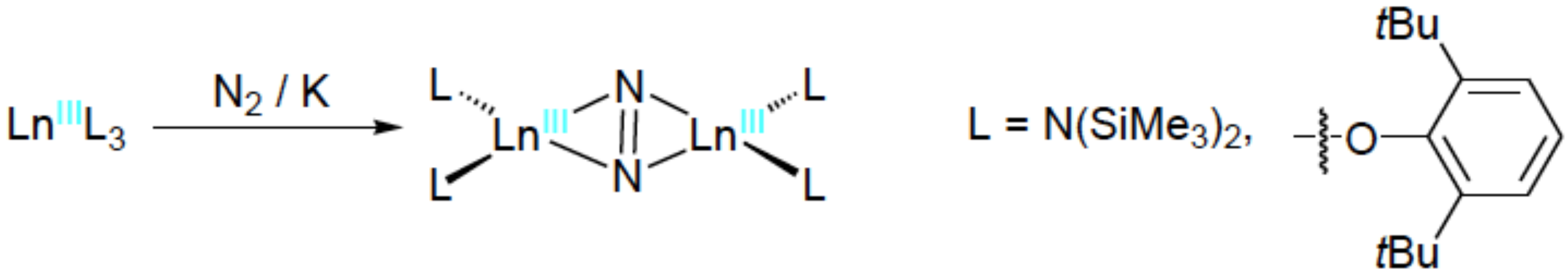
N_2 Reduction in Ln(II) Systems



Reduction of N_2 to N_2^{2-}

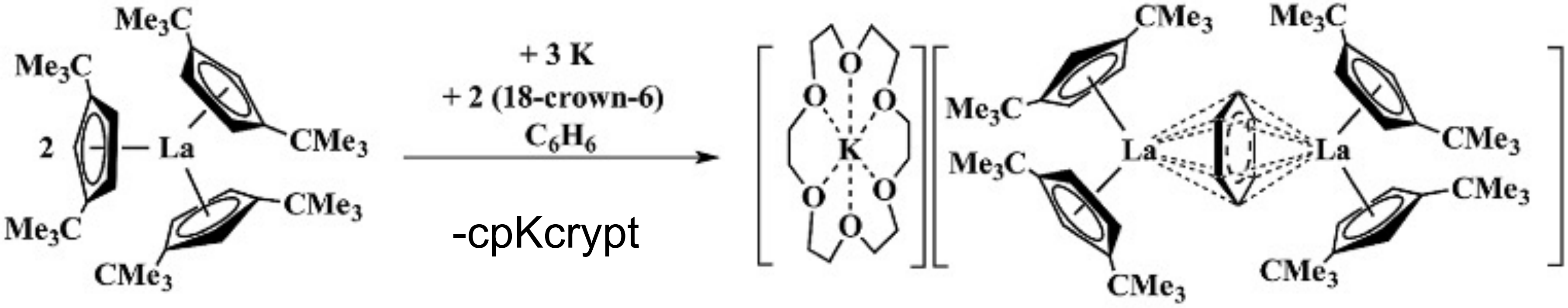
Also for Ln = Nd^{II}, Dy^{II};

not for Ln = Sm^{II}, Yb^{II}, Eu^{II} (insufficiently reducing; $Ln(NR_2)_2$ stable).



Reaction proceeds even when Ln has no readily accessible +2 oxidation state (e.g. Ln = Er, Tb, Gd). [Eº (Gd(III)/Gd(II)) = -3.9 V (vs NHE) calcd. for $4f^7$ / $4f^8$]

Reduction of $Ln^{III}Cp_3$ Complexes



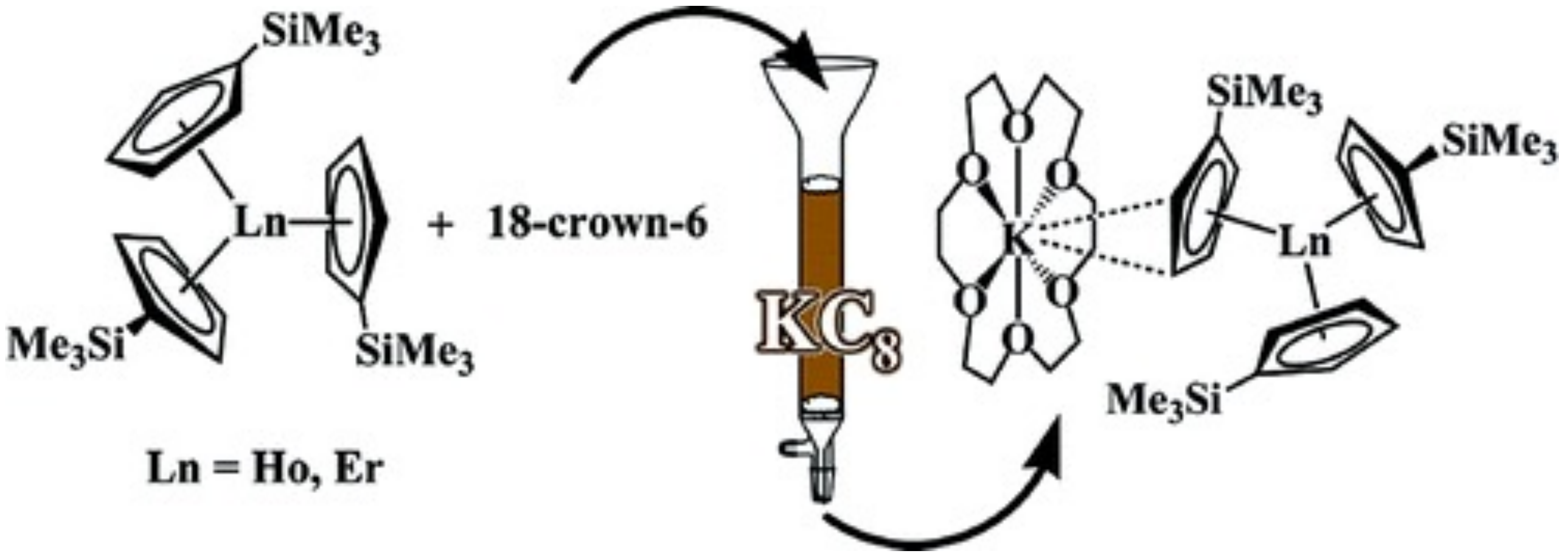
-cpKcrypt

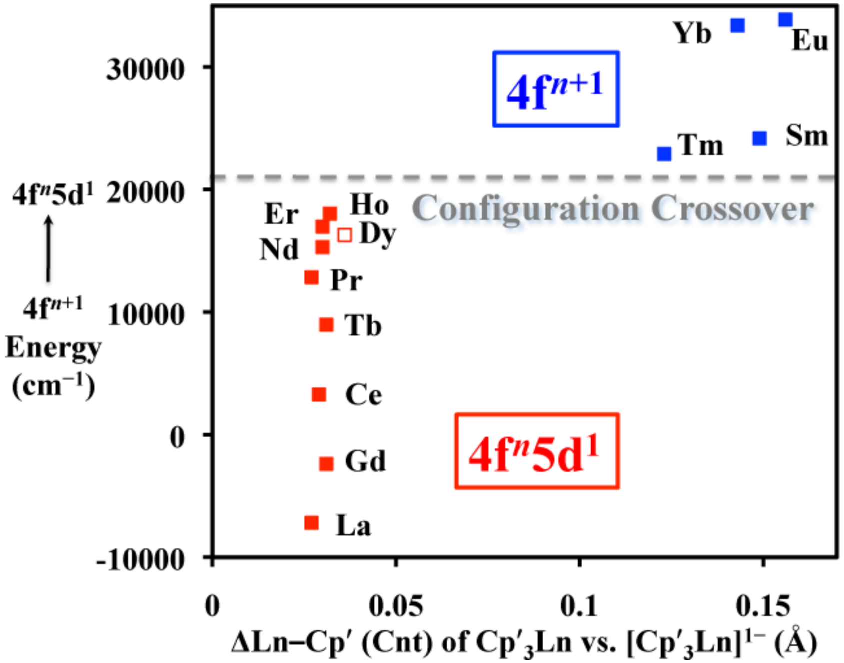
Possible electron configuration:

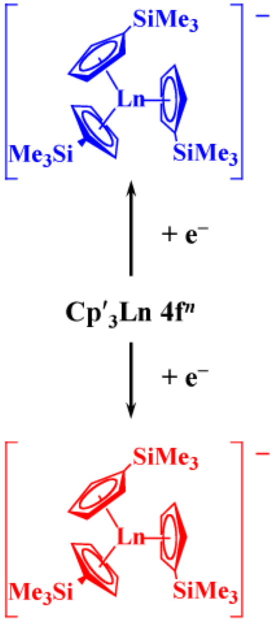
$Ln(II)$ complexes of $(C_6H_6)^{-1}$

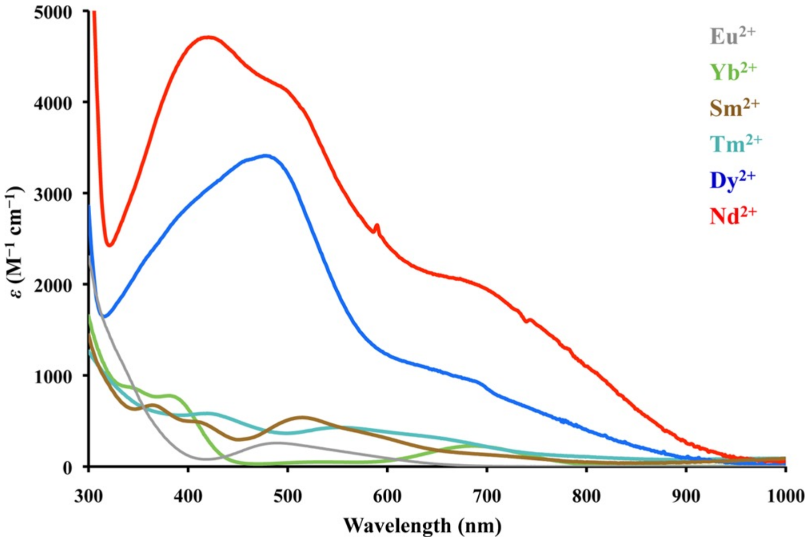
$Ln(III)/Ln(II)$ complex of $(C_6H_6)^{-2}$

Lanthanide(II) cyclopentadienyl complexes









Evans

Actinide Cp chemistry

Cp complexes are known for U in all oxidation states (+IV more common)

- **First actinide organometallics: An(IV)**

$AnCl_4 + 3\ NaCp \longrightarrow Cp_3AnCl + 3\ NaCl$ (Wilkinson, 1956)

$AnCl_4 + 4\ KCp \longrightarrow Cp_4An + 4\ KCl$ An = Th, U, Np (Fischer, 1962)

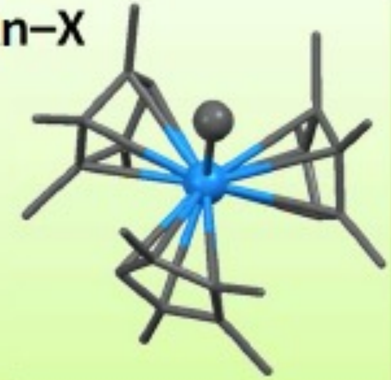
Higher coord. no. reflects larger radii:

Tetrahedral structure

- **Extensive substitution chemistry with An–X bond in $Cp_3An–X$**

$Cp_3U–Cl + MR \longrightarrow Cp_3U–R + MCl$

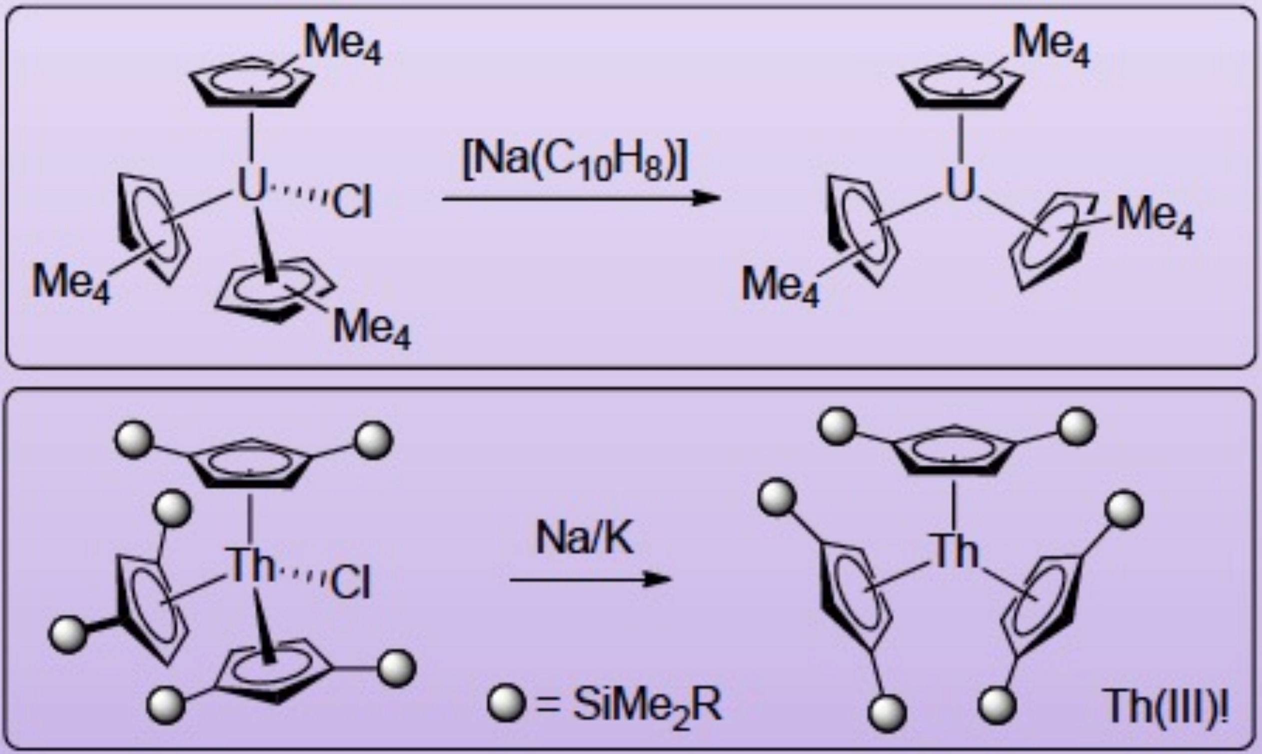
Many possible R, OR, BH_4, PPh_2, SCN



An(III) cyclopentadienyl complexes

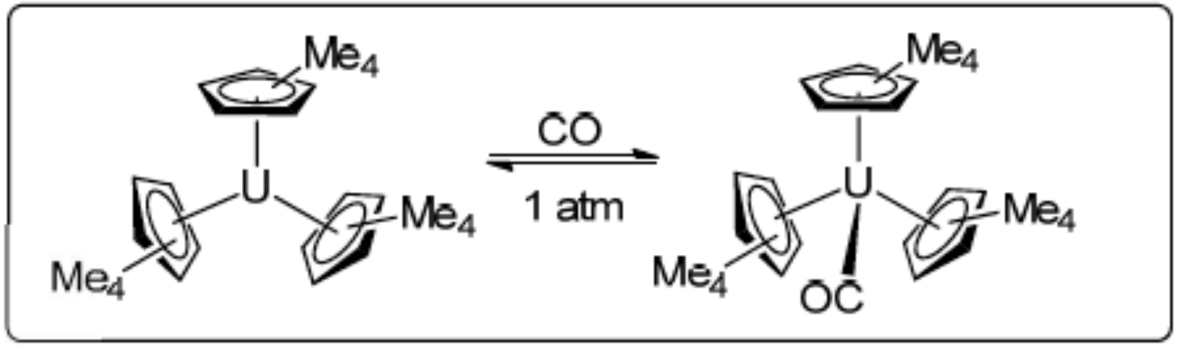
Prepared by salt methathesis or U(IV) reduction

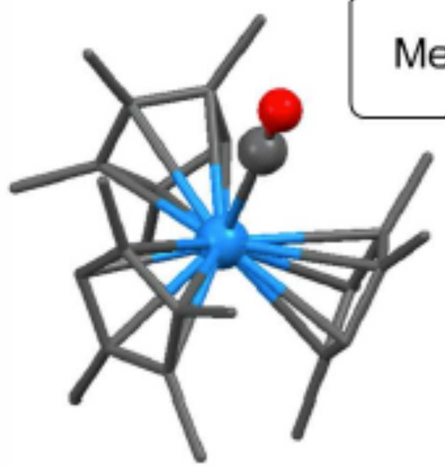
$$UCl_3 + 3NaCp \longrightarrow UCp_3 + 3\ NaCl$$



An = U, Th, Np

Uranium(III) carbonyl complexes

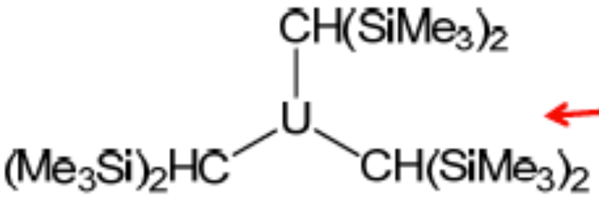




Not seen in Ln chemistry

ν(CO) = 1880 cm^{-1} indicates strong U→C back donation

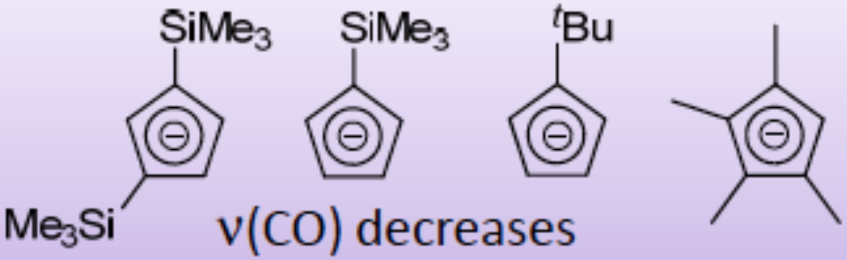
d(U–C) = 2.38 Å ← **U=C multiple bond**



← **U–C single bond**

d(U–C) = 2.48 Å

Cp'$_3$U–CO

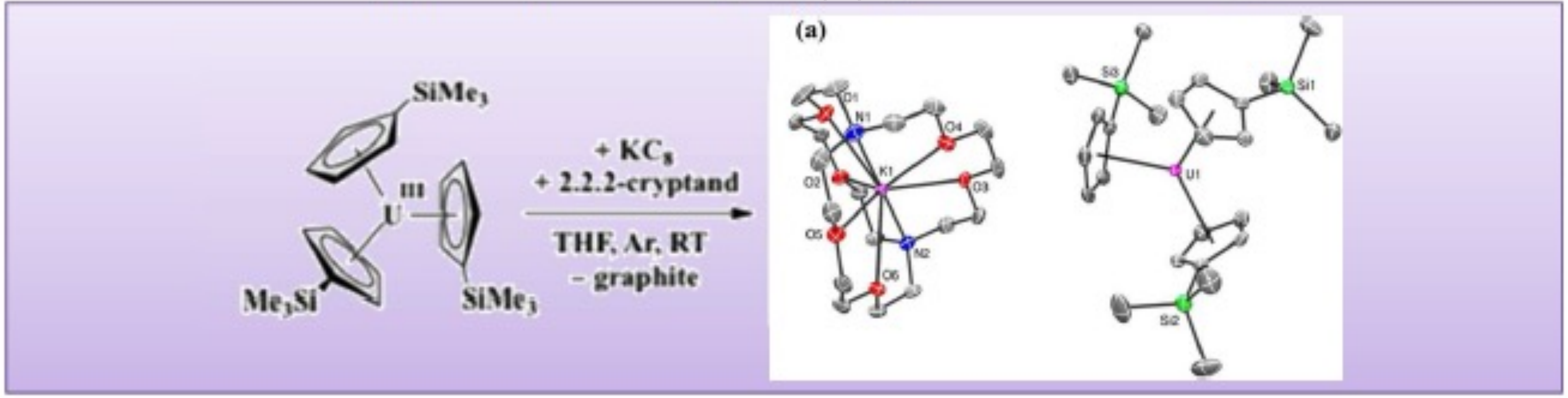


ν(CO) decreases →

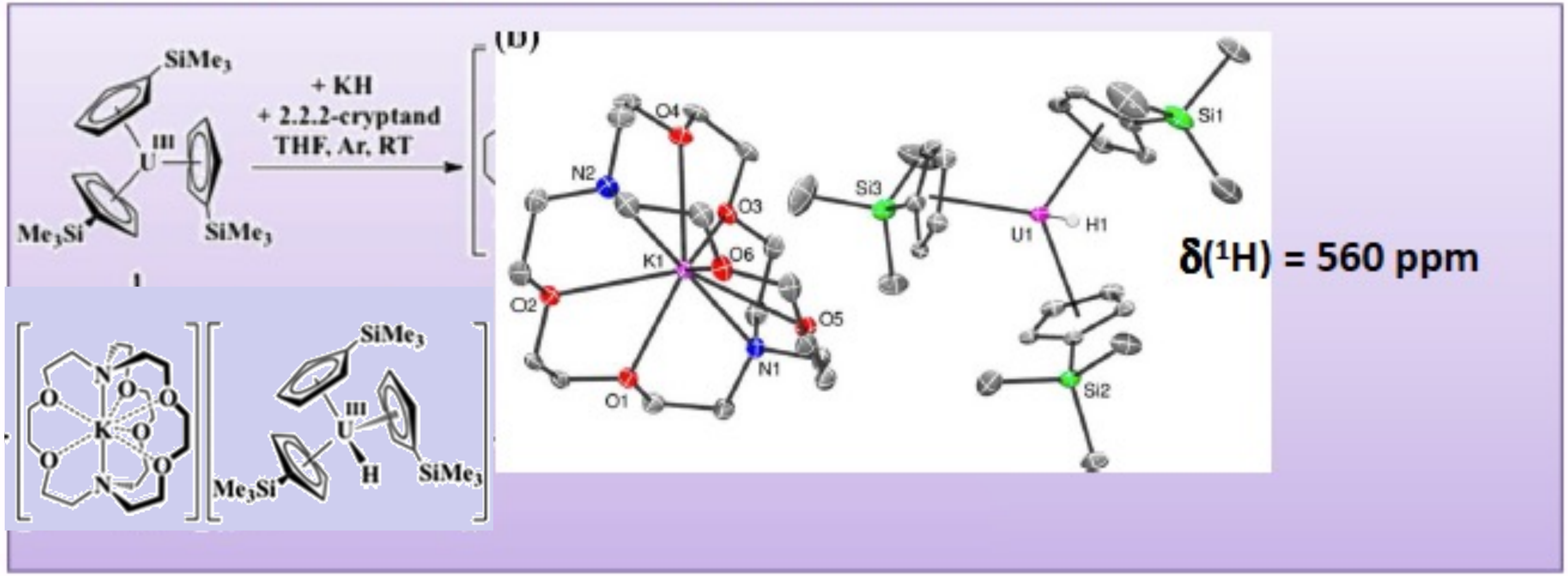
Back-bonding increases

Cp chemistry in a (very) low oxidation state: U^{2+}

First molecular exemple of uranium(II)



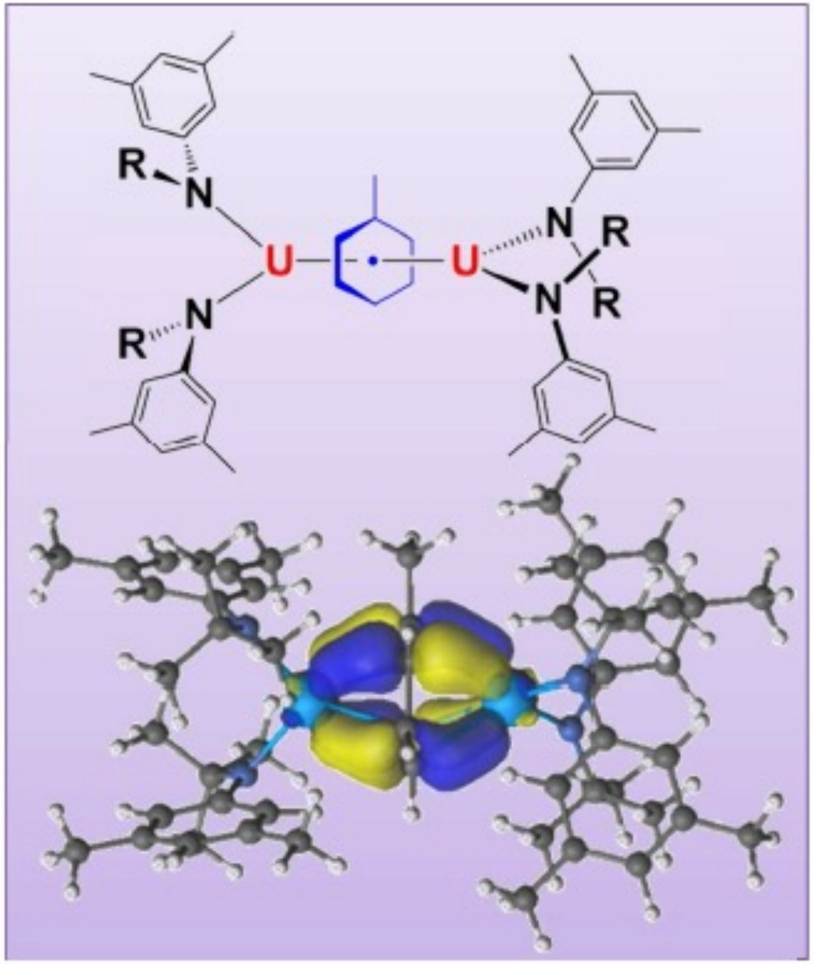
In order to prove that is U(II) and not an U(III)-H they made the U(III)-H

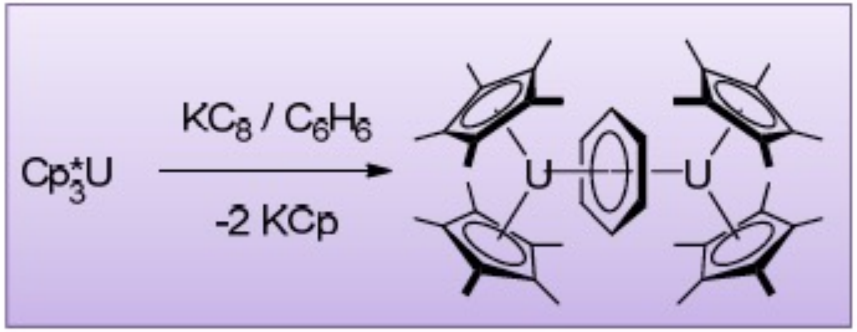


$\delta(^1H)$ = 560 ppm

Uranium arene complexes

- **Uranium forms stable η^6-arene complexes**

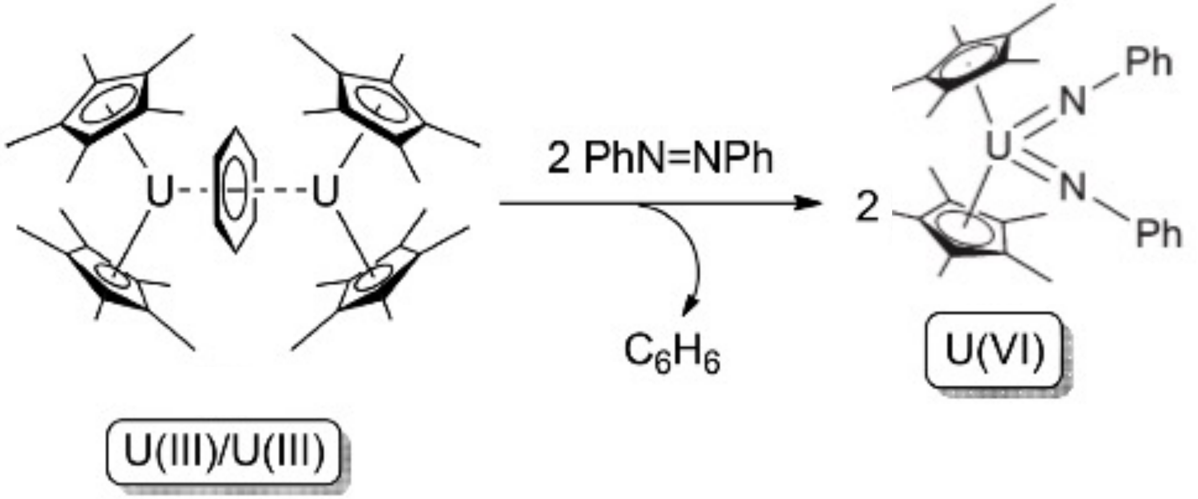




- **δ-bonding orbitals**
  between uranium 5f and arene π*
- **XANES spectroscopy consistent with**
  two U(III) and [arene]$^{2-}$
- Is not U(II)!!!

Obtained by reduction of $[UI(N(RAr)_3]$
with KC8

Ligand based reactivity of uranium arene complexes



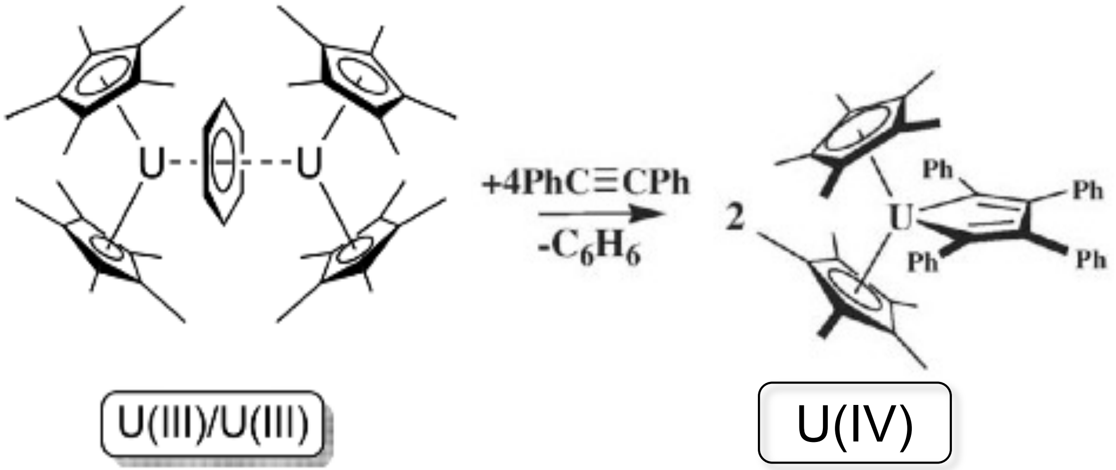
U(III)/U(III)

U(VI)

$$2\ \mathrm{PhN{=}NPh} \xrightarrow{8\ e^-} 4\ \mathrm{PhN}^{2-}$$

$$2\ \mathrm{U(III)} \xrightarrow{-\ 6\ e^-} 2\ \mathrm{U(VI)}$$

$$(C_6H_6)^{2-} \xrightarrow{-\ 2\ e^-} C_6H_6$$



U(III)/U(III)

U(IV)

$$4\mathrm{PhC{\equiv}CPh} + 4e^{1-} \longrightarrow 2(C_4Ph_4)^{2-}$$

$$2U^{3+} \longrightarrow 2e^{1-} + 2U^{4+}$$

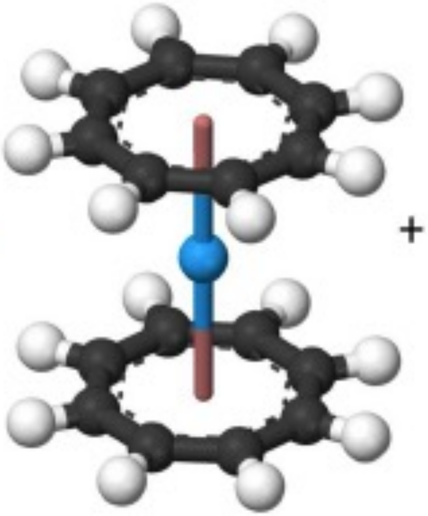
$$(C_6H_6)^{2-} \longrightarrow 2e^{1-} + C_6H_6$$

Actinide cyclo-octatetraene (η^8-COT) complexes

- **Uranocene:**

Streitweiser, 1968

$UCl_4 + 2\,[K_2(COT)] \rightarrow$



$+ 4\,KCl$

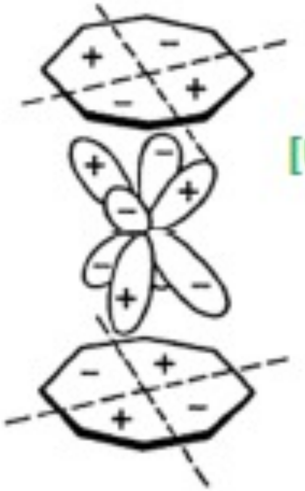
- D8h symmetry in solid state; COT rotation in solution
- Resistant to hydrolysis!

An(III) sandwich complexes (KSolvent)[M(RC_8H_7)$_2$] are known for U, NP, Pu, Am

Cp2Fe

Significant U–C covalence

δ bonding
The involvement
of 5f is not certain
perhaps 6d



[U(COT)$_2$]

Two electron Oxidative Addition and Reductive Elimination Reactions: not common in An chemistry

$$L_nM^m + X\text{-}Y \xrightleftharpoons[\text{R.E.}]{\text{O.A.}} L_nM^{m+2}(X)(Y)$$

$$2\ L_nM^m + X\text{-}Y \xrightleftharpoons[\text{R.E.}]{\text{O.A.}} L_nM^{m+1}(X) + L_nM^{m+1}(Y)$$

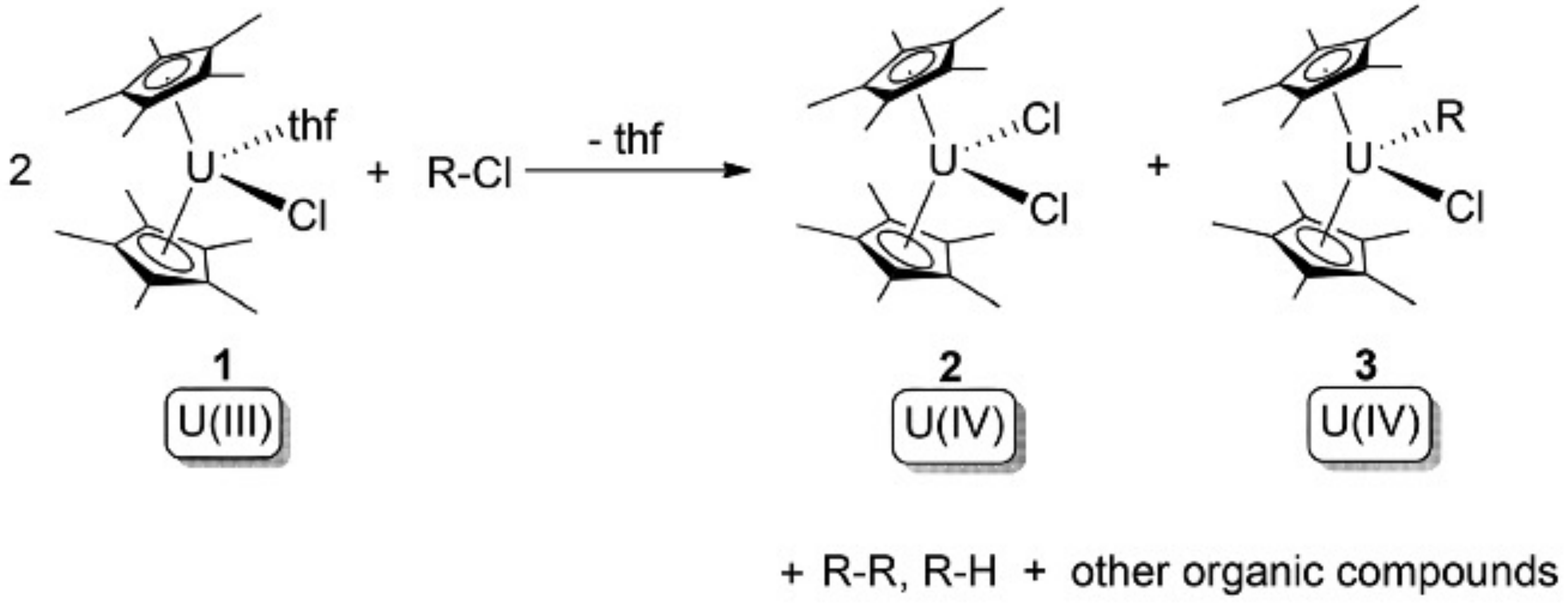
AO: (i) increment of oxidation state of metal; (ii) cleavage of an X–Y bond; (iii) formation of M-X and M-Y bonds

Organo-5f chemistry is dominated (as for 4f) by salt metathesis, insertion reactions of unsaturated bonds, 1-electron redox processes, and σ-bond metathesis due to their highly polarising nature but OA and RE are more common for uranium

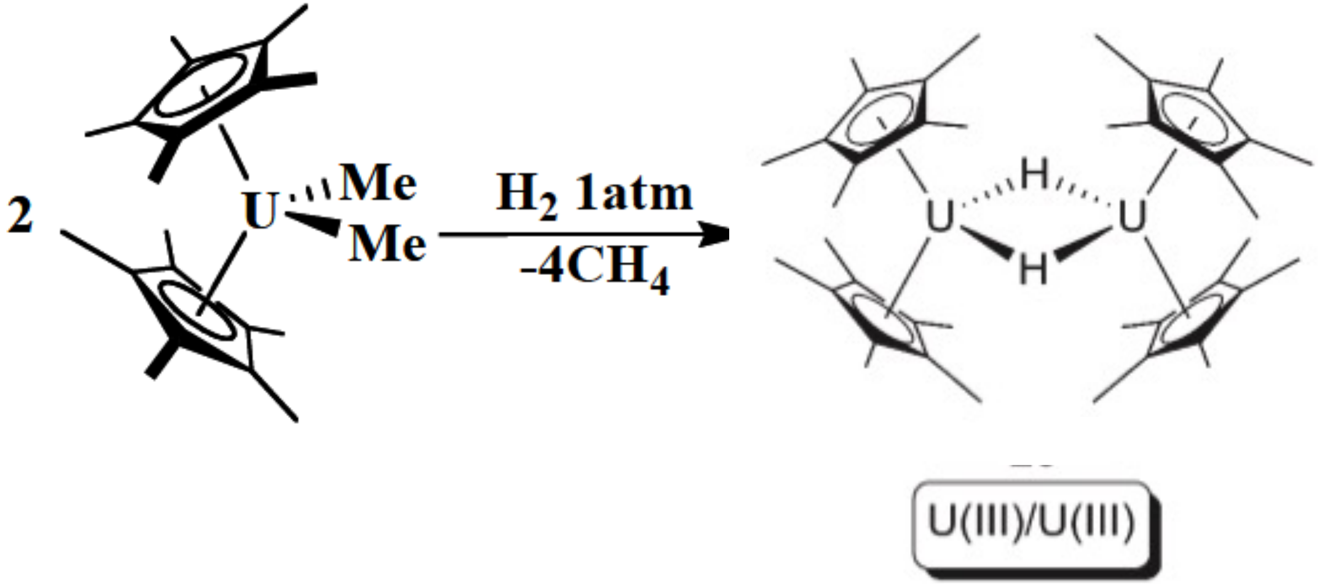
Liddle, Dalton Trans., 2015, 44, 12924–12941

Exemple of oxidative addition in uranium species

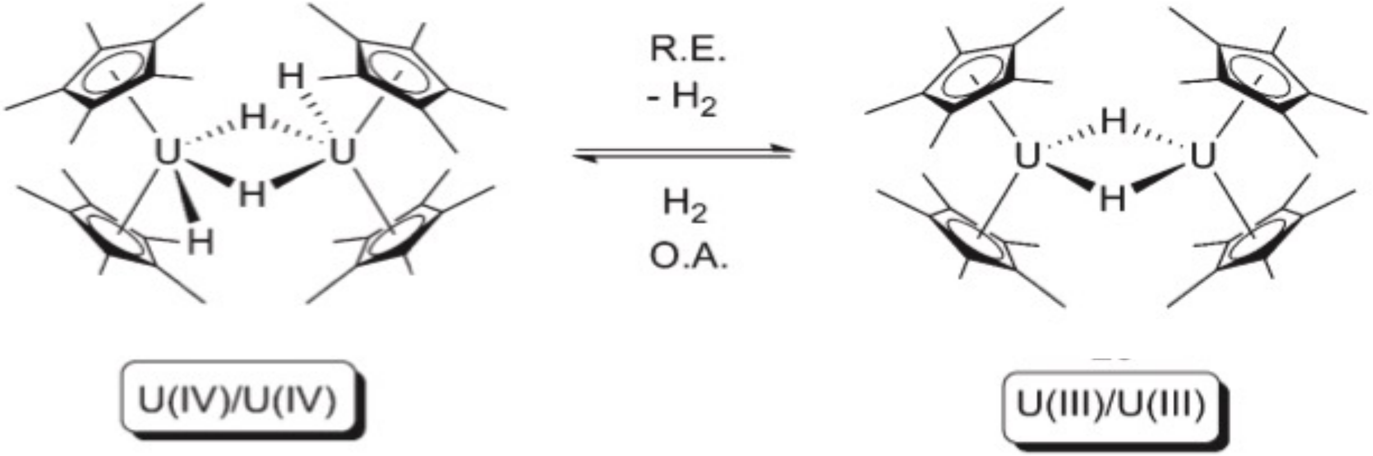
U^{3+}/U^{4+} interconversion



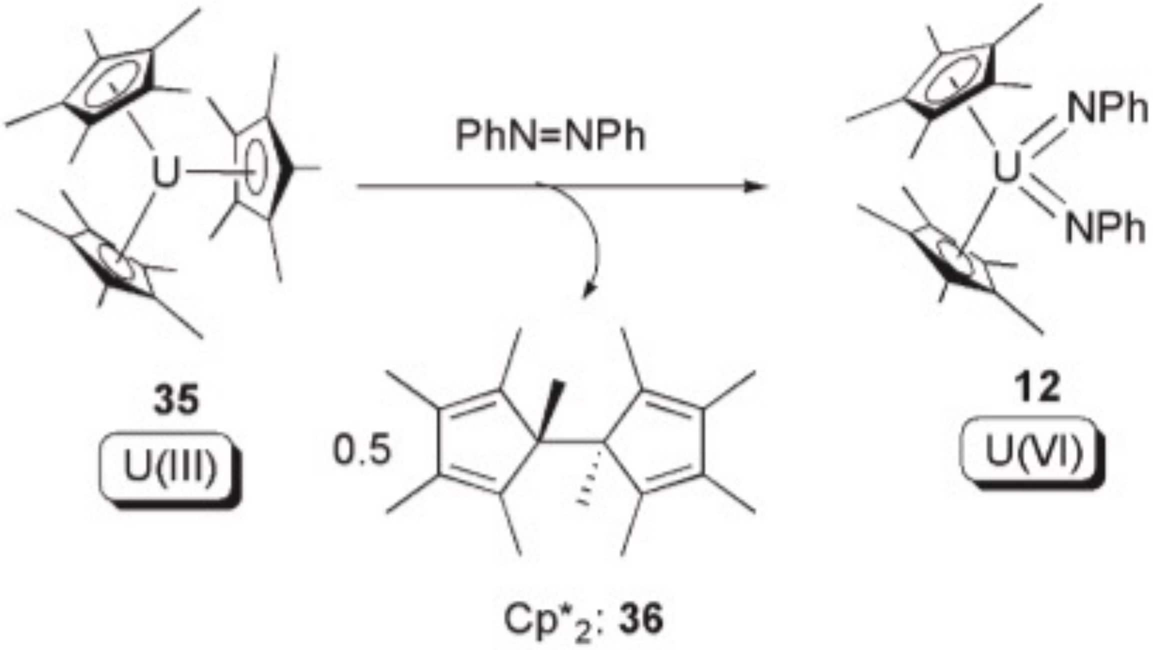
Exemple of Reductive Elimination in Uranium Species



U^{4+}/U^{3+} interconversion: Bimetallic RE



Oxidative addition of azobenzene to U(III), with the assistance of 1-electron donation from a Cp*⁻ ligand (SIR).



35 U(III)

12 U(VI)

Cp*$_2$: **36**

$$\mathrm{PhN{=}NPh} \xrightarrow{4\,e^-} 2\ \mathrm{PhN^{2-}}$$

$$\mathrm{U(III)} \xrightarrow{-\,3\,e^-} \mathrm{U(VI)}$$

$$\mathrm{Cp^{*-}} \xrightarrow{-\,1\,e^-} \mathrm{Cp^{*}\cdot} \xrightarrow{\text{dimerisation}} \mathbf{36}$$

Summary

- Organometallic Ln/An complexes are very unstable to water and oxygen
  Because they are hard acids and C donors are soft bases

- Anionic Ligands Alkyl, aryl, allyl, vinyl, acetylide: $[R]^-$;$[Cp]^-$; $[COT]^{2-}$
- Complexes of neutral π-acceptor ligands such as CO or alkenes unknown for Ln
  CO complexes of An exist (back-bonding interaction)

- Ionic bonding Ln-C and An-C has a very polar character resulting in metallation and insertion reactions (in d metals back-bonding and covalent M-C)

-Alkyl and Cp adopt terminal and bridging binding modes (η^5 , η^2 , η^1)

-Synthesis by salt methatesis from halide or alkoxide, amides

- $LnCp_2Cl$ complexes can be useful starting materials for heteroleptic alkyl complexes

- C-H activation , insertion reactions , σ-bond methatesis, metallation reactions
  Are common for these complexes

- Rare exemples of OA and ER in An organometallic complexes

- Ligand based reactivity (SIR and reduced arenes)