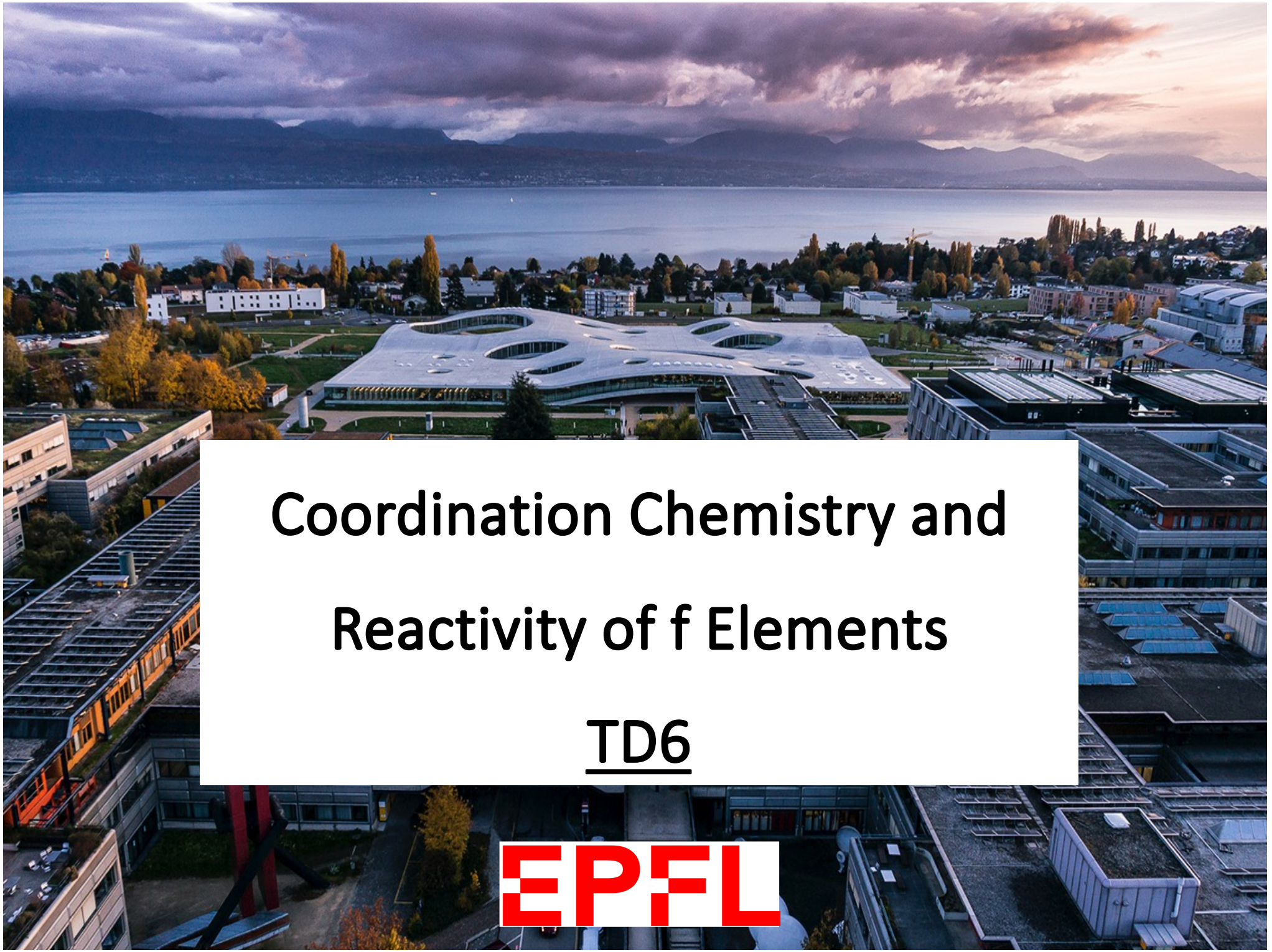

Coordination Chemistry and Reactivity of f Elements

TD6

EPFL

Question 1:

1) Draw the reaction schemes of [Cp_3La] and [$^{Me4}Cp_3U$] with CO. Explain the origins of the observed differences in reactivity.

2) Describe the bonding between the metals and CO in the products of these reactions and suggest possible techniques that allow to elucidate the bonding in these complexes.

Answer 1:

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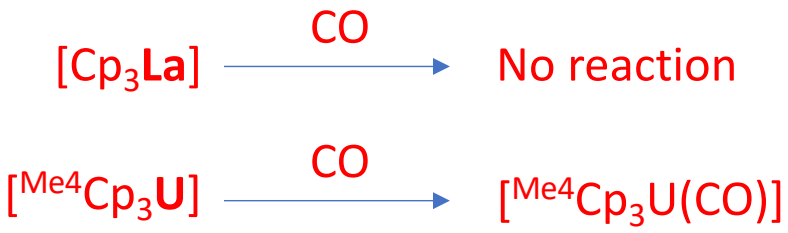


Lanthanide(III) cannot form covalent interactions (backbonding)

Actinide(III) can have covalent contributions (required for CO bonding)

Answer 1:

2) Describe the bonding between the metals and CO in the products of these reactions and suggest possible techniques that allow to elucidate the bonding in these complexes.

The U—CO bonding involves a **weak σ-bonding** interaction and a **backbonding** interaction

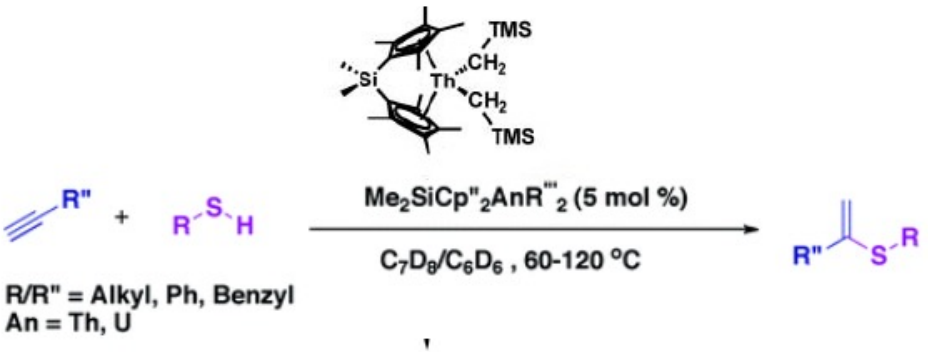
- IR spectroscopy: decrease in CO stretching compared to free CO

- X-Ray SC diffraction. Longer C—O distances compared to free CO and shorter U-C bond Compared to U-C single bonds

Question 2:

1) Indicate the two major reaction patterns in organometallic actinide chemistry

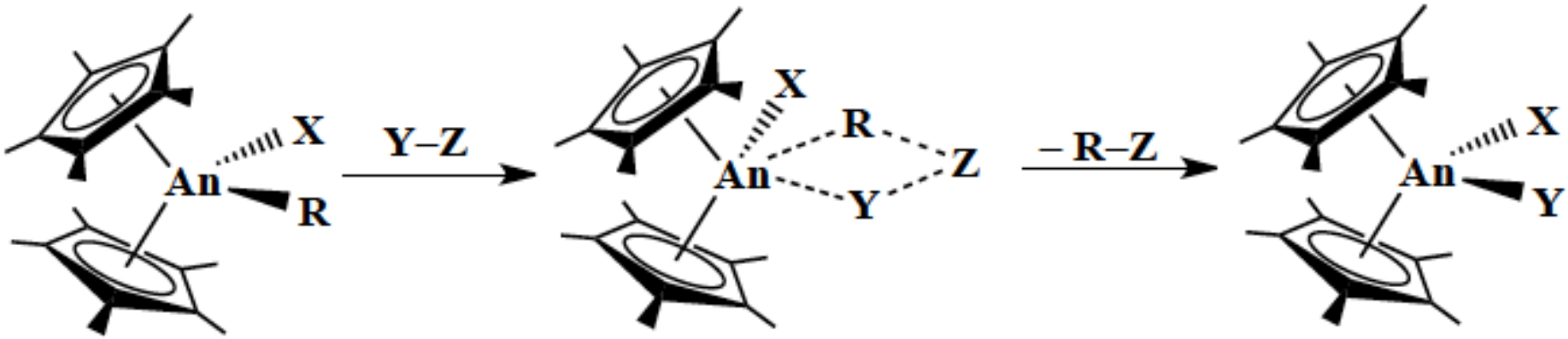
2) Draw a possible mechanism for the following catalytic reaction



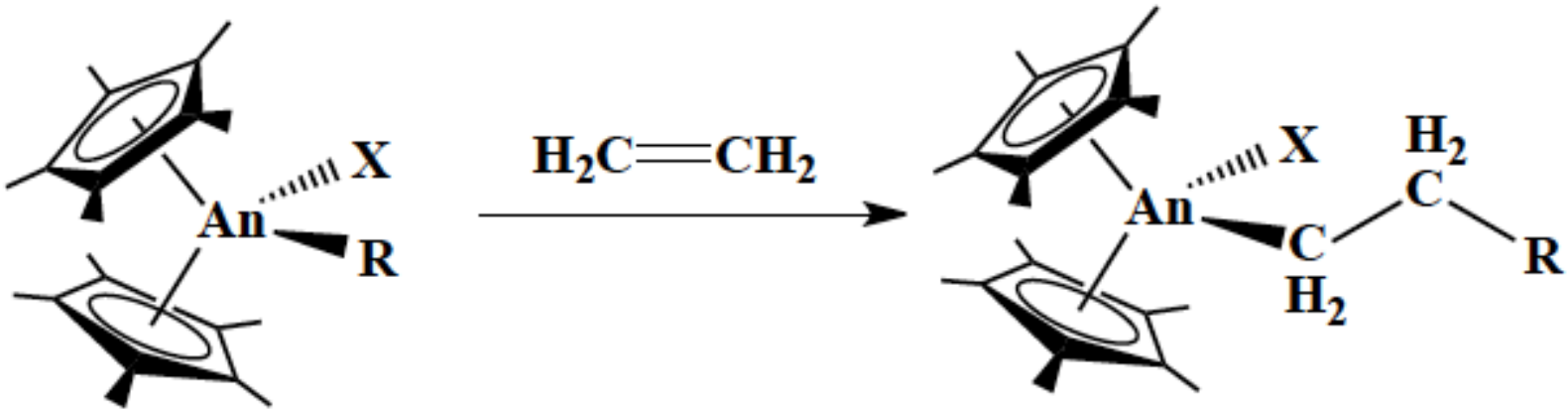
Answer 2:

1) Indicate the two major reaction patterns in organometallic actinide chemistry

Sigma-bond metathesis



Insertion Reactions:



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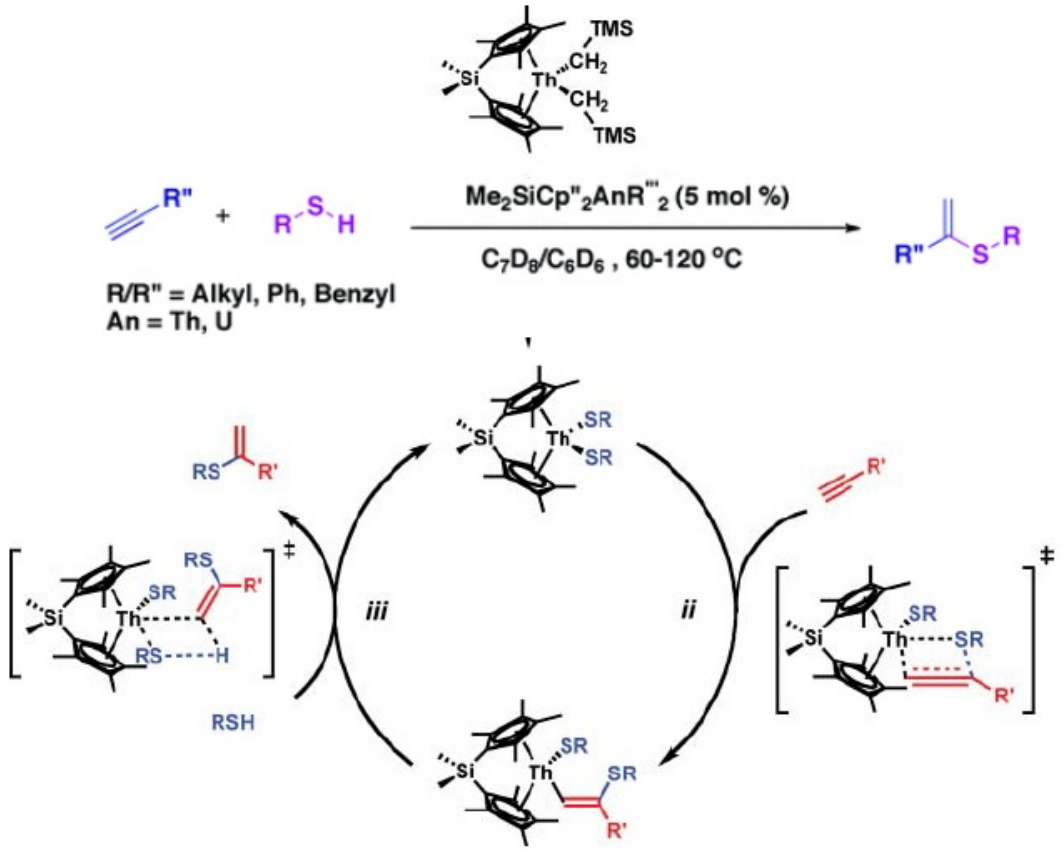
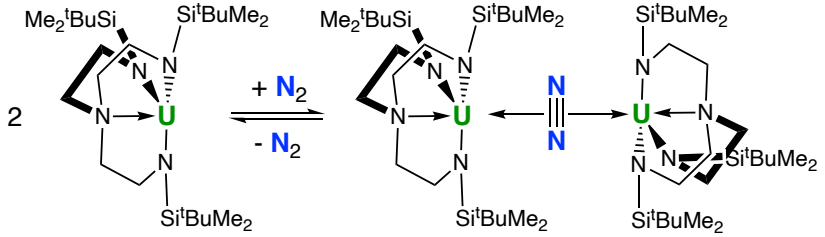


Question 3:

1) For the six complexes below assign the oxidation state of the uranium atoms and of the N atoms. Describe what type of reaction is occurring in each case.

a)



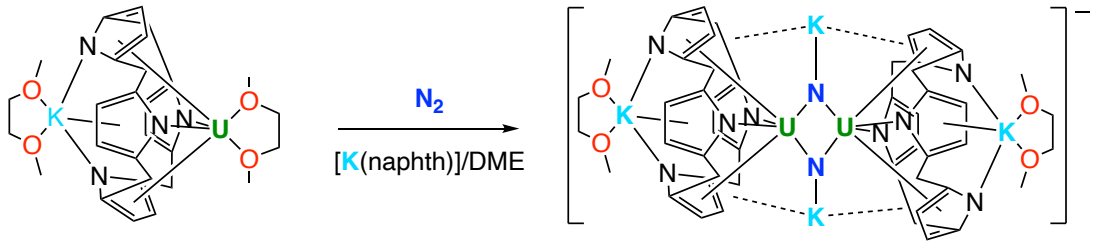
N≡N 1.109(7) Å

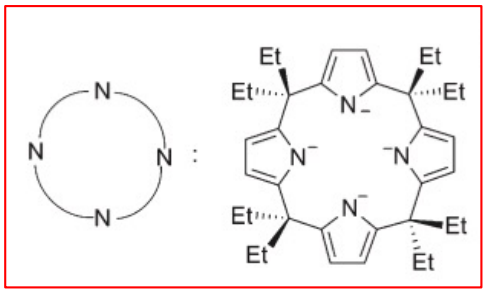
N≡N free 1.0975 Å

b)

N=N 1.163(19) –1.236(5) Å

c)





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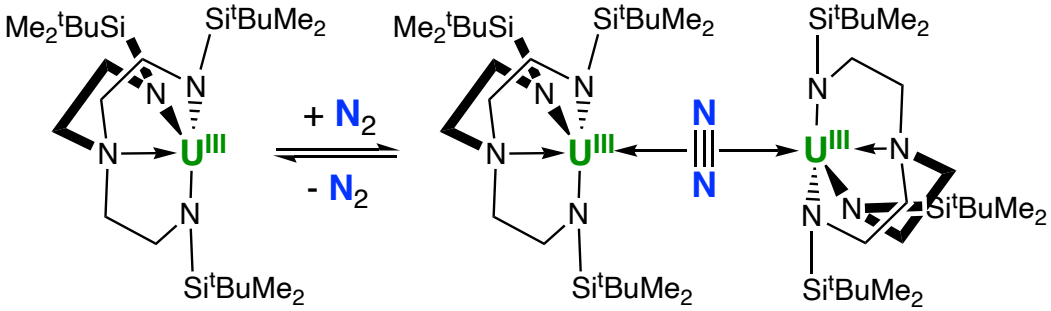


N≡N bond distance: 1.109(7) Å

N≡N free 1.0975 Å

Scott et al., *JACS*, **1998**, 120, 32

- No change in oxidation state of the U centers
- N_2 binding

Answer 3:

1) For the six complexes below assign the oxidation state of the uranium atoms and of the N atoms. Describe what type of reaction is occurring in each case.

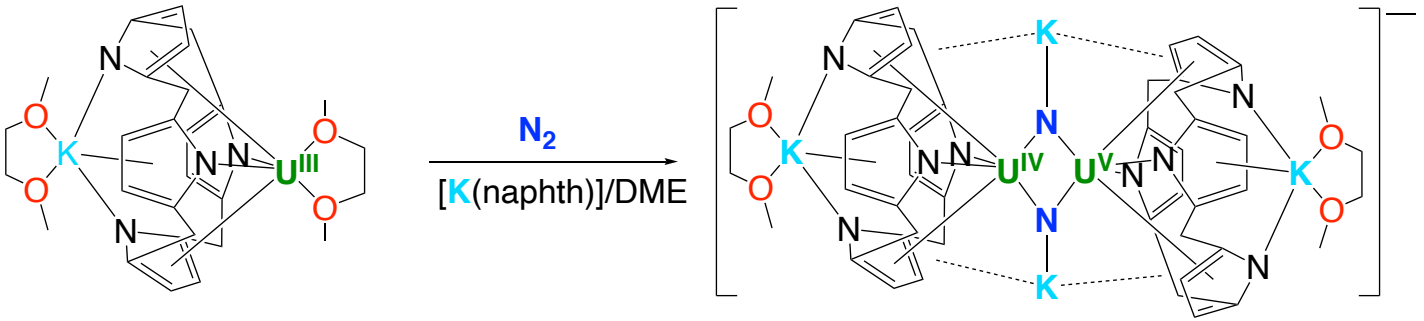
N=N bond distance: 1.163(19) – 1.236(5) Å

N≡N free 1.0975 Å

- U(III) to U(IV)
- N_2 to N_2^{2-}
- N_2 reduction to diazenido

Answer 3:

1) For the six complexes below assign the oxidation state of the uranium atoms and of the N atoms. Describe what type of reaction is occurring in each case.



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

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

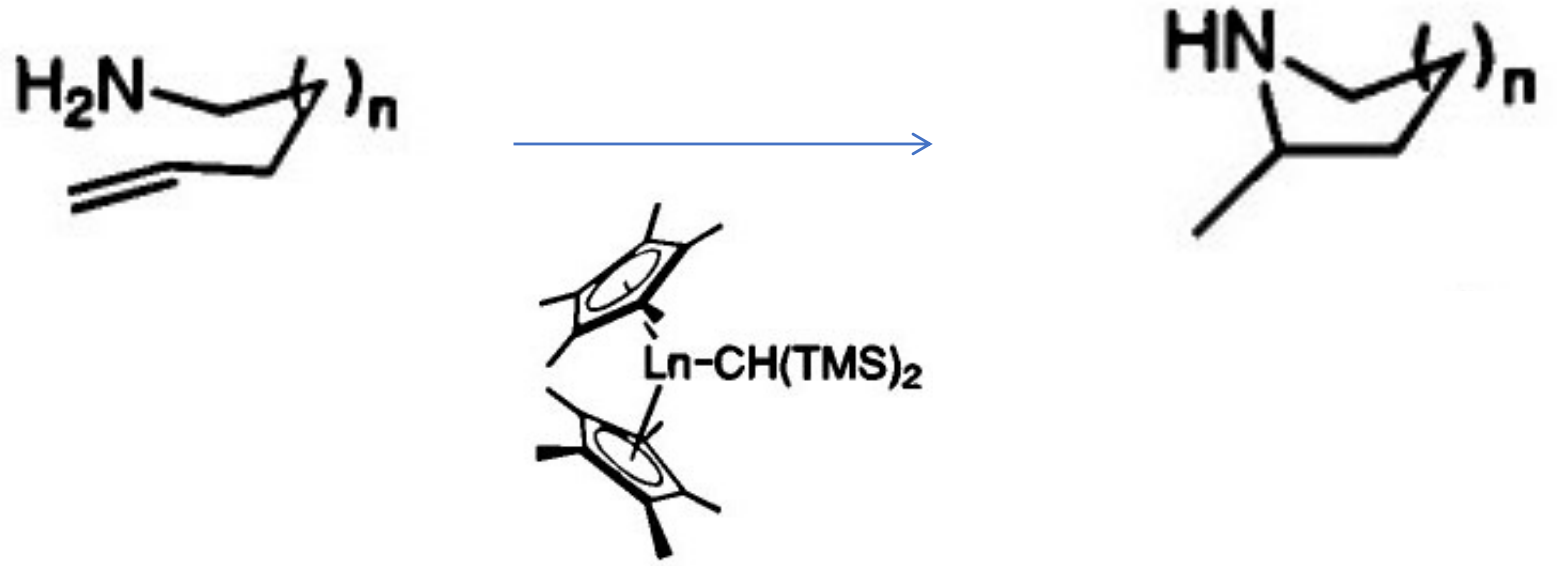
$$U(III) \xrightarrow{-1\ e^-} U(IV)$$

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

- One U(III) to U(V)
- One U(III) to U(IV)
- N_2 reduction to nitrides

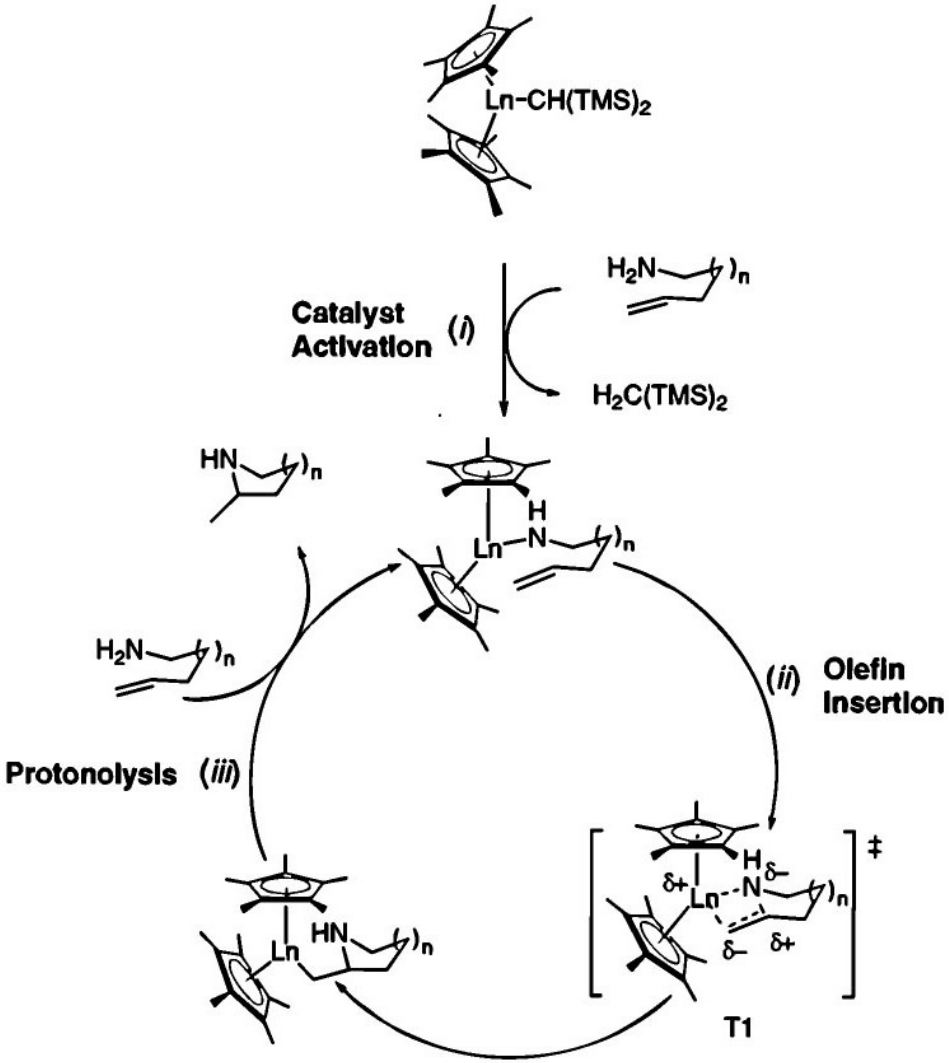
Question 5:

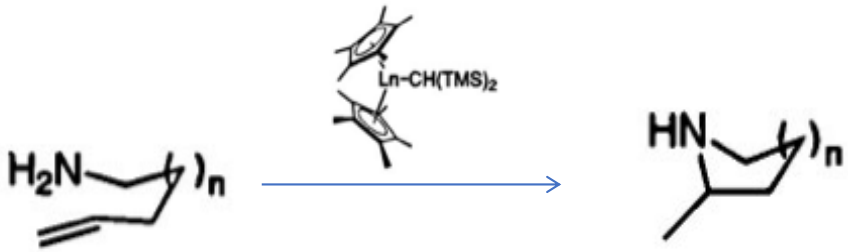
1) Describe the catalytic mechanism of the hydroamination reaction below.



Answer 5:

1) Describe the catalytic mechanism of the reaction.

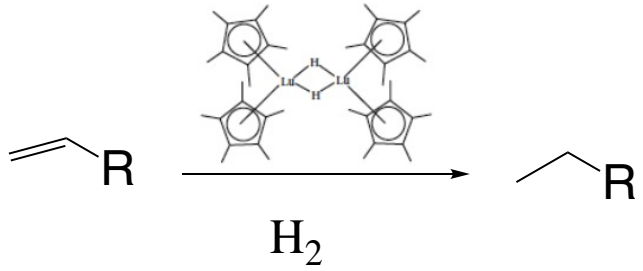




Hydroamination reaction catalysed by lanthanide bis Cp complexes

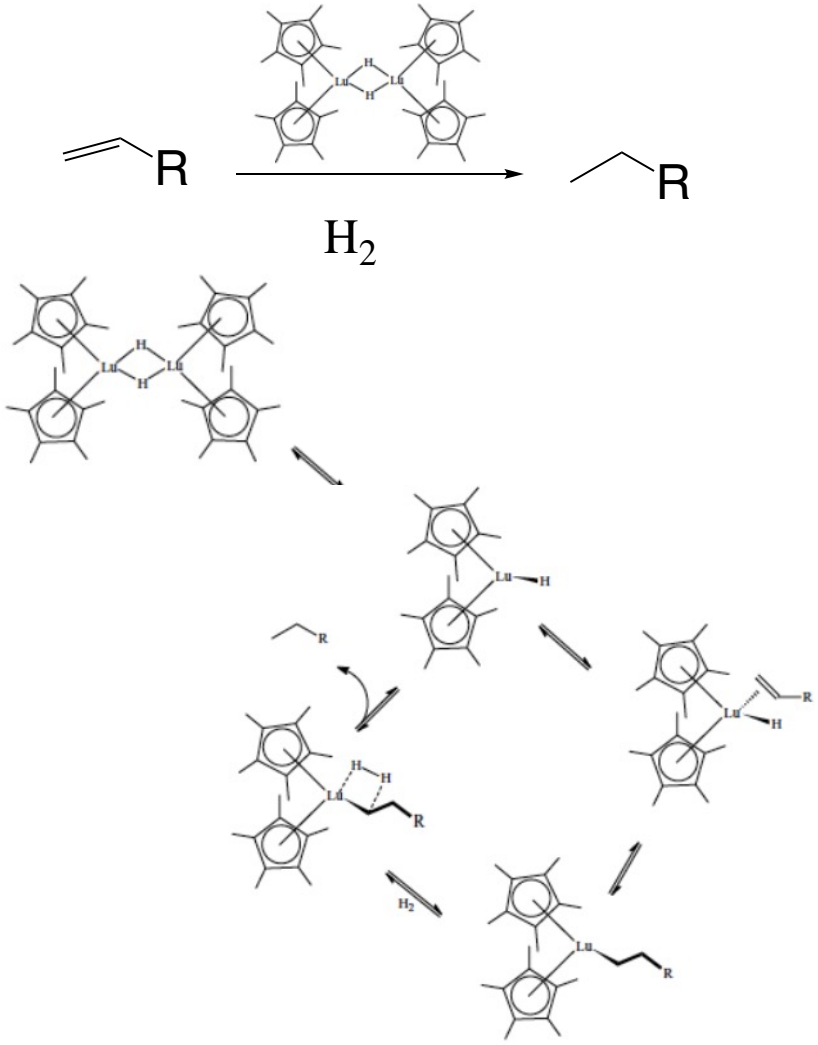
Question 6:

2) Identify the mechanism of the following lanthanide catalysed reaction



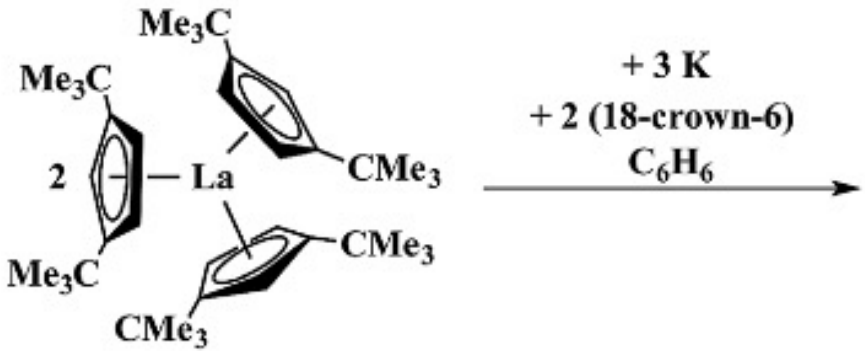
Answer 6:

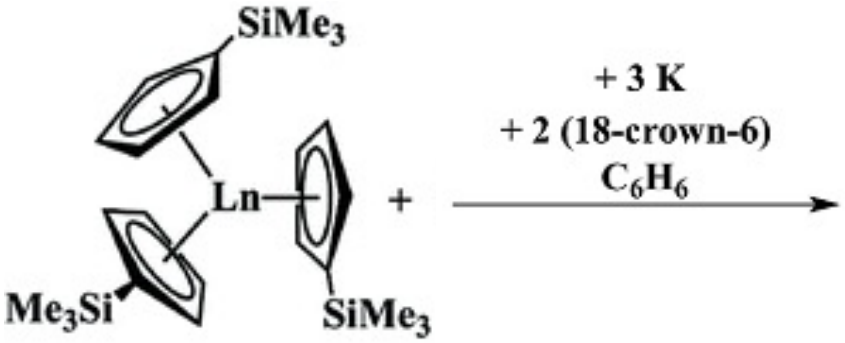
2) Identify the mechanism of the following lanthanide catalysed reaction



Question 7:

1) Draw the structures of the products of the following reactions and suggest possible reasons for different reactivity.





Ln = Ho, Er

Answer 7:

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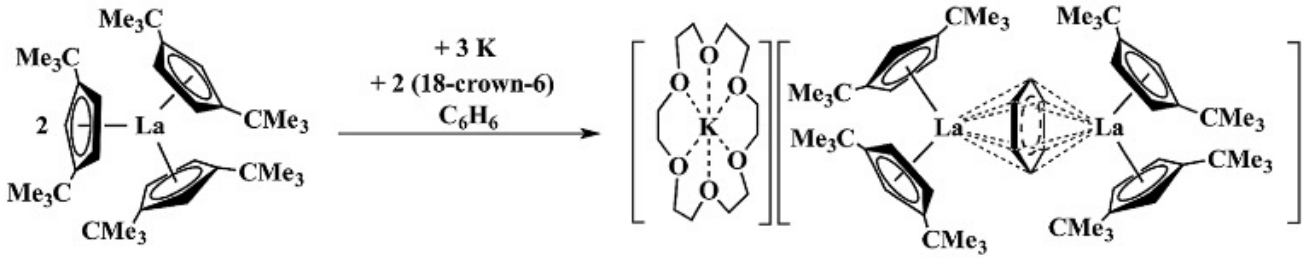
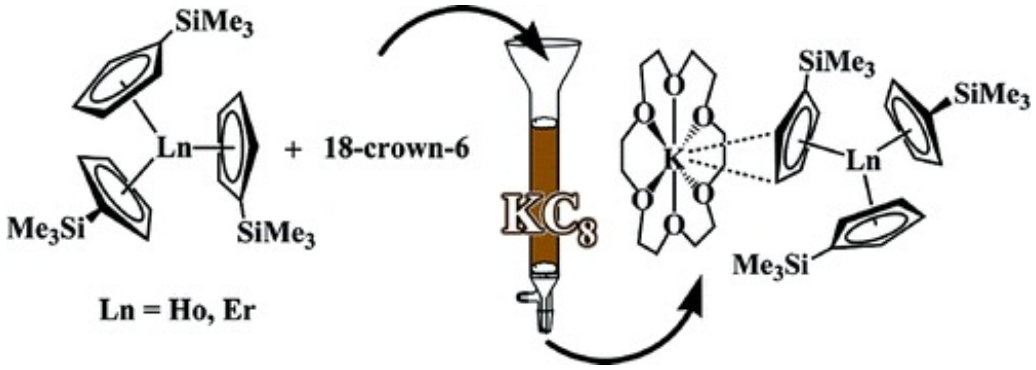


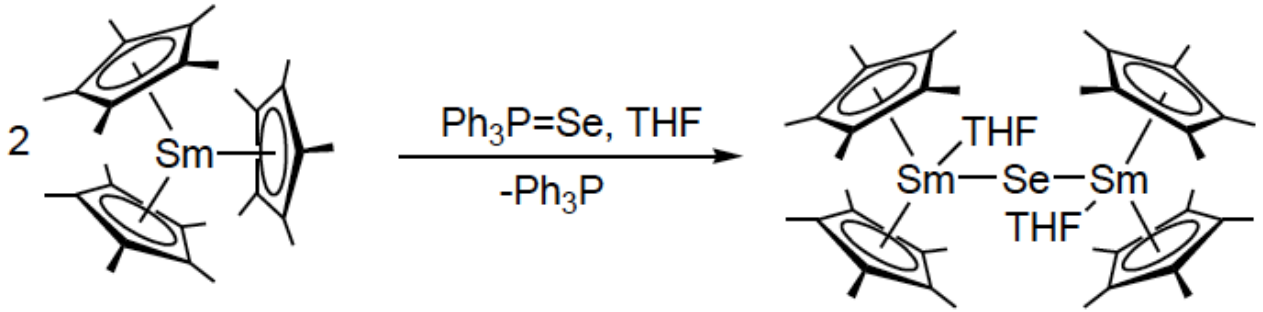
- Dinuclear
- Ln(II) complex of $(C_6H_6)^{-1}$
- EDG

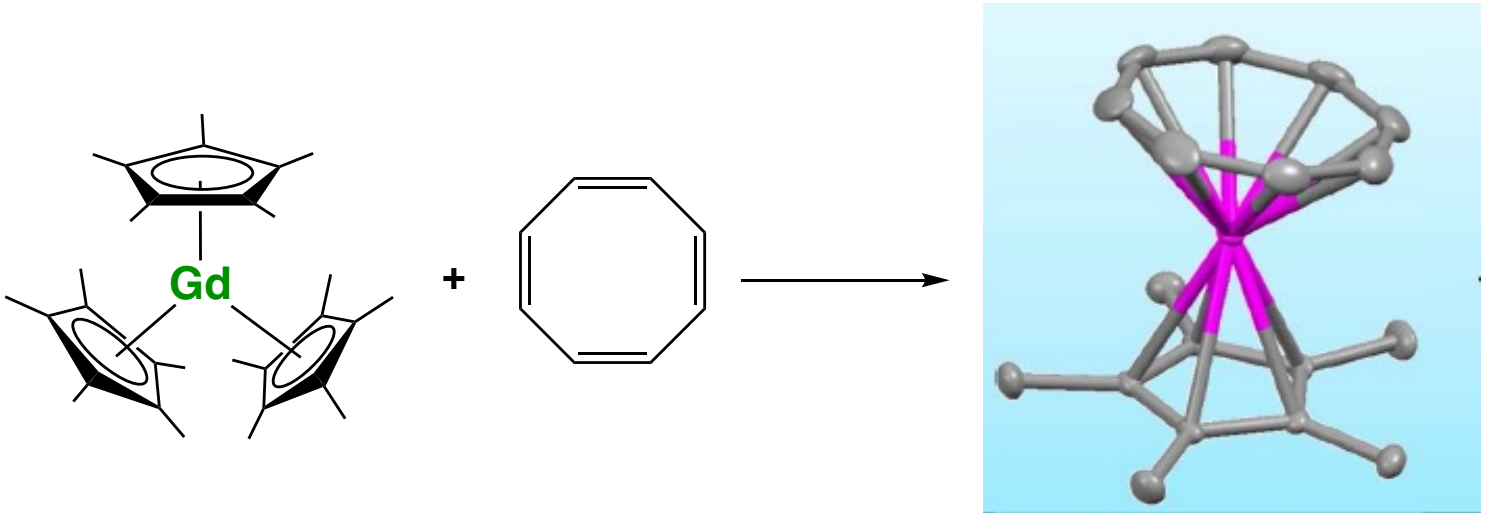


- Ln(II) complex
- K interacts with Cp
- EWG

Question 8:

1) In the two redox reactions below the oxidation state of the metal is unchanged. Can you explain how is the substrate reduced?





Indicate the name of the type of reaction above and the additional product.

Answer 8:

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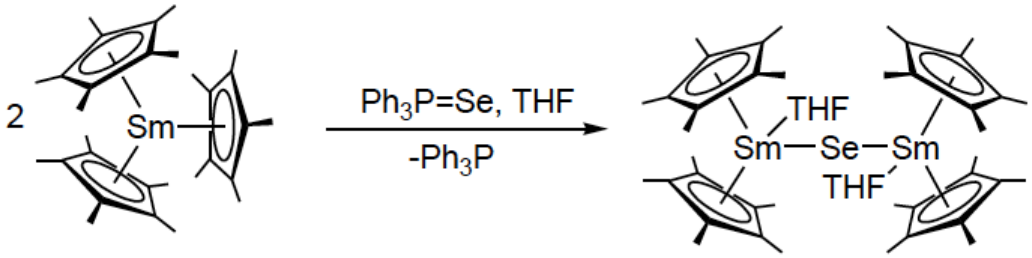
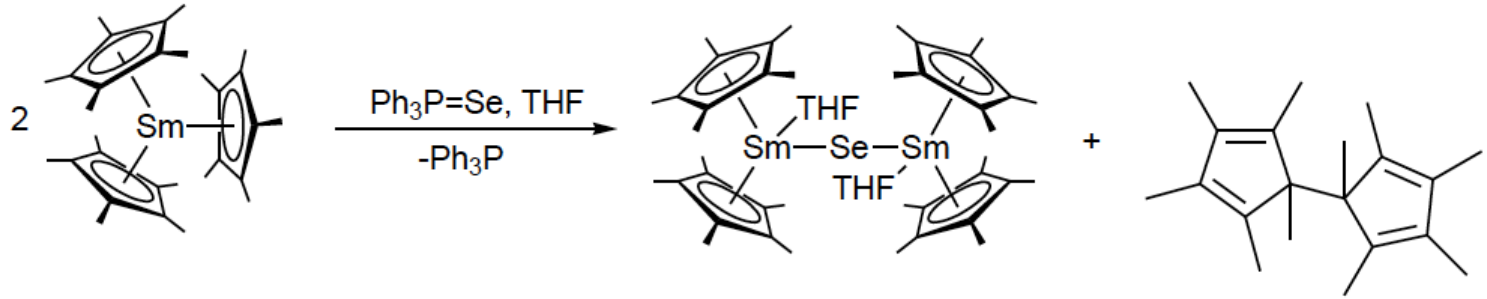


Sm(III) → Sm(III) - What is the reducing agent?



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

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