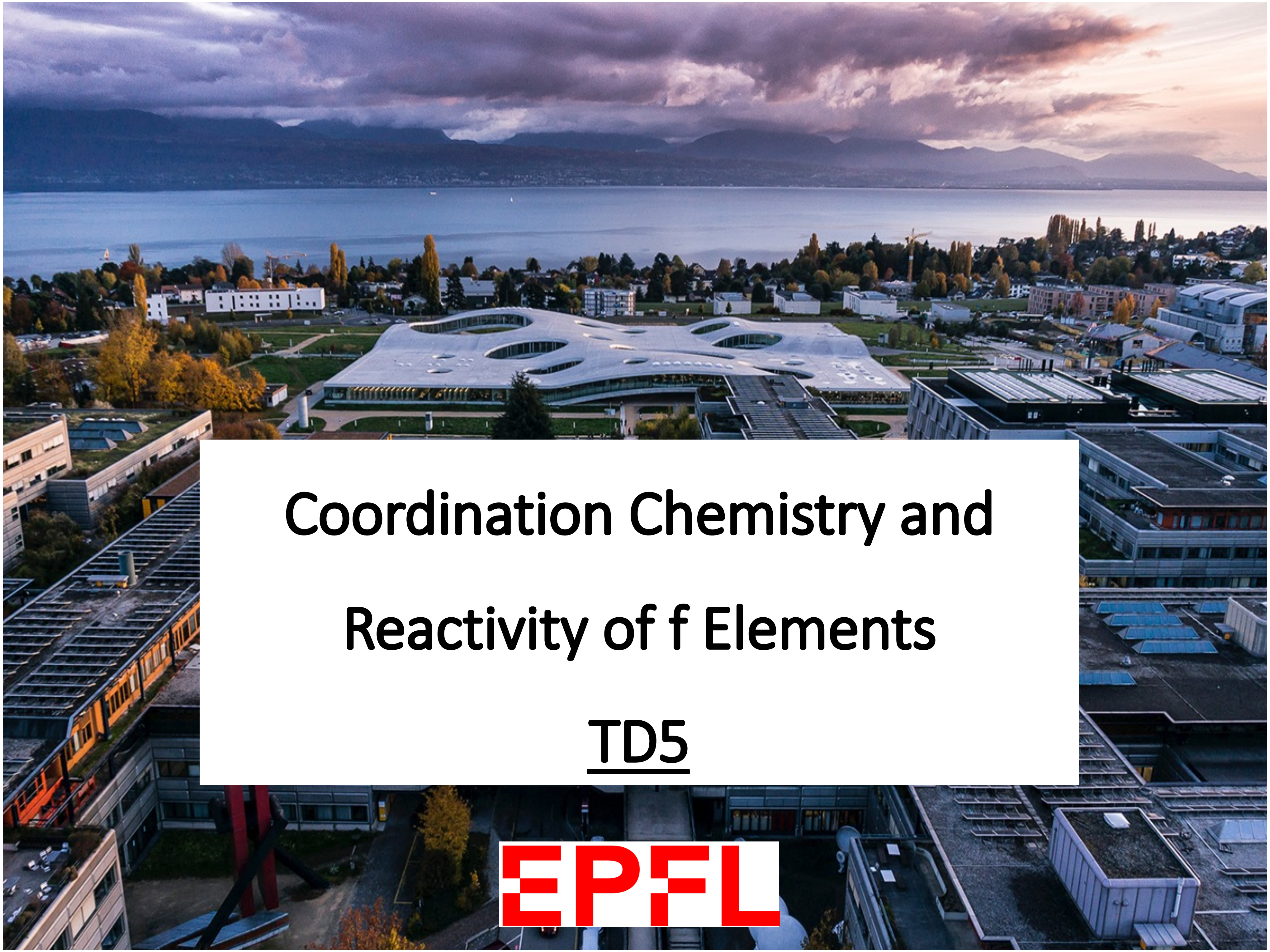


Coordination Chemistry and Reactivity of f Elements

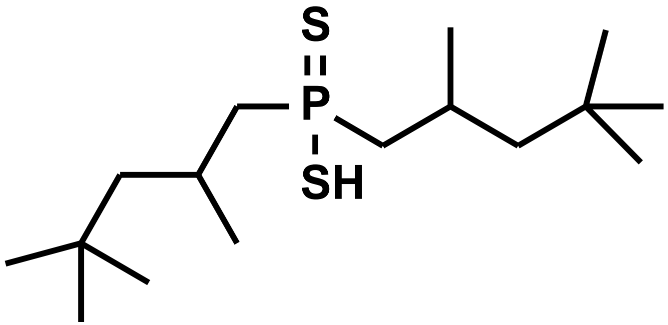
TD5

EPFL

Question 1

1) Indicate the main steps of spent nuclear fuel reprocessing.

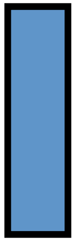
2) Indicate in which step the molecule below has been used and why.



Answer 1

1) Indicate the main steps of spent nuclear fuel reprocessing.

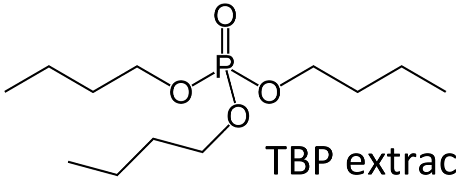
1st stage: extraction of U and Pu



HNO_3 7 M

nitrates

3
months
in water



TBP extraction
in kerosene (PUREX)

Other fission
products + highly radioactive
minor An

Np

$[UO_2(NO_3)_2(TBP)_2]$
$[Pu(NO_3)_4(TBP)_2$

Fe^{II}

$[UO_2(NO_3)_2(TBP)_2]$
Not reduced stay
in organic layer

$Pu^{III}(aq)$ not
complexed by TBP

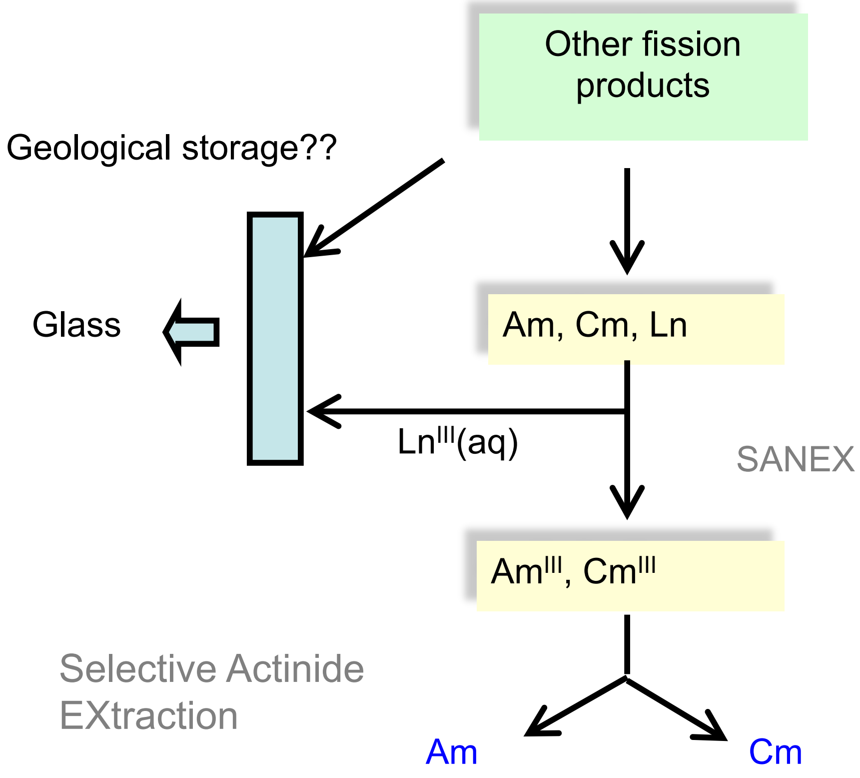
Operational
In France and USA

UO_2

PuO_2

Answer 1

1) Indicate the main steps of spent nuclear fuel reprocessing.



Other fission products

Geological storage??

Glass

Am, Cm, Ln

$Ln^{III}(aq)$

SANEX

Am^{III}, Cm^{III}

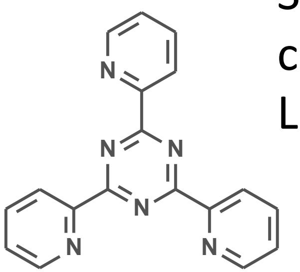
Selective Actinide EXtraction

Am

Cm

DIAMEX process

Amides can be used to separate highly radioactive actinides such as Am^{3+} or Cm^{3+} and Ln^{3+} from other less radioactive fission products like transition metals



Soft donor ligands could be used in Ln(III)/An(III) separation

2) Indicate in which step the molecule below has been used and why.

It is used in the **selective actinide extraction of Am(III) with respect to Ln(III)**. The selectivity is due to the fact that the soft S donor atoms interact better with An(III). This is due to the larger participation of 5f orbitals compared to 4f orbitals in covalent bonding.

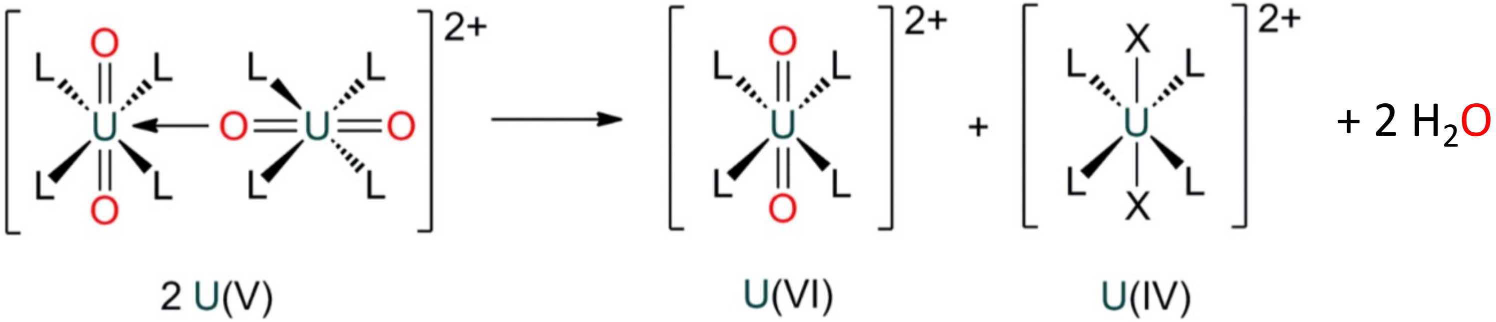
Question 2

1) Uranyl (V) is not stable. Indicate why and indicate the intermediates involved in the decomposition.

2) Explain how to stabilize uranyl(V).

Answer 2

1) Uranyl(V) is not stable. Indicate why and indicate the intermediates involved in the decomposition.



- Inner sphere disproportionation
- Cation-cation interaction
- CCI stronger in U(V)
- More rapid in water

Answer 2

2) Explain how to stabilize uranyl(V).

- Blocking cation-cation interaction:

a) sterically bulky ligand

b) highly coordinating solvents

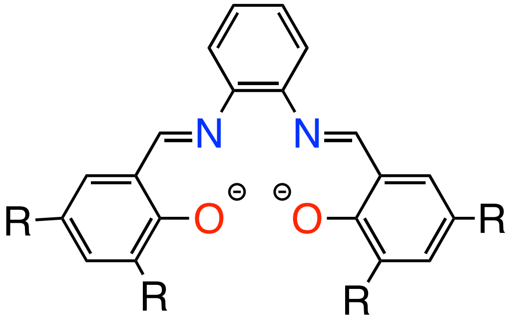
c) using high denticity ligands

to prevent coordination of uranyl oxo groups

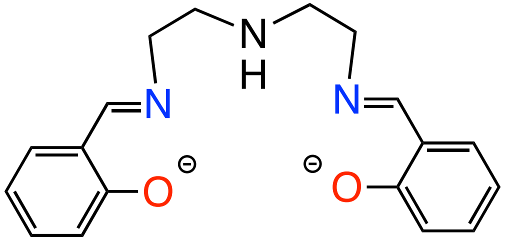
d)Capping alkali ions

- Avoiding protic solvents

Stable cation-cation complexes disproportionate when proton is added to the basic uranyl(V) oxo group eliminating H_2O



R: H, ^{t}Bu



R: H, ^{t}Bu

Question 3

a) Give the ground state for a U(IV) ion

b) Calculate the magnetic moment for a U(IV) complex using the Russel-Sanders spin for spin orbit coupling scheme.

c) Compare the value to measured value for measured for $[U(NCS)_8]^{4-}$: 2.9 μ_B

And explain the difference

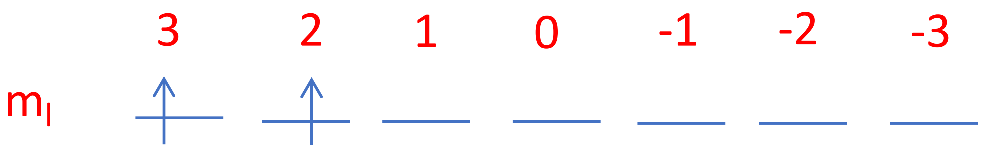
d) Explain why complexes of uranyl(VI) are not diamagnetic but show a week paramagnetism

e) The room temperature magnetic moment cannot be used to identify the +IV, and +III oxidation states of uranium. How can they be differentiated?

Answer 3

a) Give the ground state of a U(IV) ion.

U: [Rn] $5f^3 6d^1 s^2$ **U^{4+}: [Rn] f^2**



S = 1

L = 5

J = L – S = 4

0	1	2	3	4	$\boxed{5}$	6
S	P	D	F	G	$\boxed{H}$	I

Ground state: $^{2S+1}L_J$ $\Rightarrow$ $^3H_4$

Answer 3

b) Calculate the magnetic moment of a U(IV) complex using the Russel-Saunders spin orbit coupling scheme.

S = 1   L = 5   J = L – S = 4

$$\mu_{eff} = \frac{\sqrt{3RT \cdot \chi_M}}{N_A \cdot \beta} = 2{,}828\sqrt{\chi_M \cdot T}$$

$$\mu_{eff} = \mu_j = g_J\sqrt{(J(J+1)} \quad \boxed{= 3.57\ \mu_B}$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = 0.8$$

Answer 3

C) Explain the difference of this theoretical value with the measured value for $[U(NCS)_8]^{4-}$: 2.9 μ_B. $\neq 3.57\ \mu_B$

- In the Russell-Saunders scheme the **spin-orbit coupling is weaker** than the interelectronic repulsion term.

- For 5f elements the **spin-orbit coupling is stronger** than for 4f elements

- In 5f orbitals the electrons are not so “core-like” as in 4f and crystal field is more important

- So the approximation of the Russel-Saunders scheme in some cases does not work for 5 f elements.

- In addition often excited states mix with the ground state at high temperature

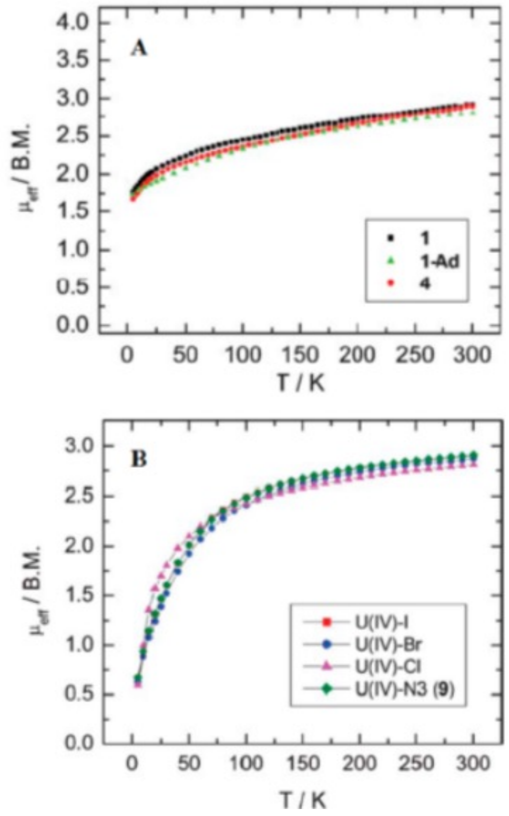
Answer 3

D) Explain why complexes of uranyl(VI) are not diamagnetic but show a week paramagnetism.

- They often display **temperature-independent paramagnetism (TIP)**
  → mixing of excited states with the ground state.

Answer 3

E) How can the +IV and +III oxidation states of uranium be differentiated using magnetometry ?



U(III)

U(IV)

- Magnetic moment at RT doesn't allow to differentiate U(III) or U(IV)
- The measure of the magnetic susceptibility in function of the temperature allows to differentiate +III and + IV
- U(IV): magnetic moment tend to 0 at low temperature
- U(III): smaller decrease with T is found

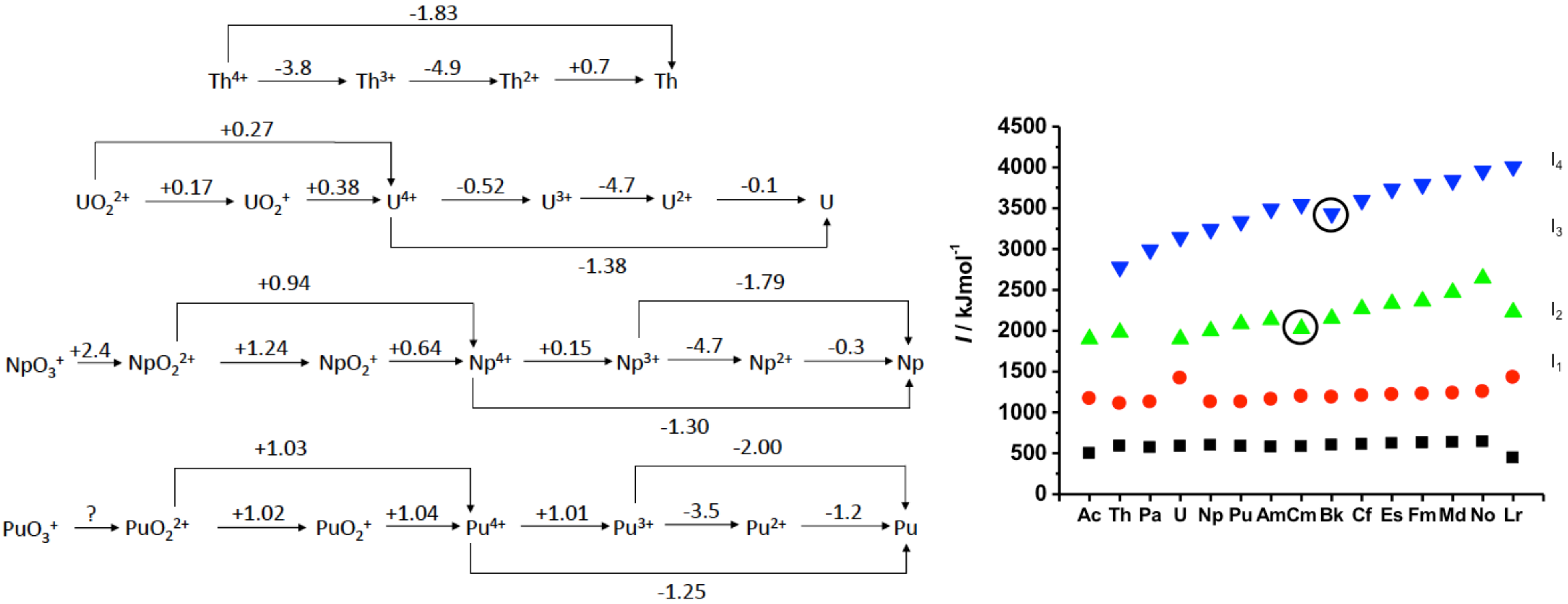
Kindra, D. R.; Evans, W. J., Magnetic Susceptibility of Uranium Complexes. *Chem. Rev.* **2014,** *114*, 8865-8882

Question 4:

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

a) Recall the most common oxidation states of actinides and rationalize their stability using the provided information on ionization energies and redox potentials.

b) Indicate the oxidation states stable in ambient conditions.



![EPFL]

Answer 4:

89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

a) Recall the most common oxidation states of actinides and rationalize their stability using the provided information on ionization energies and redox potentials:

The first four ionization energies of Th are lower than Zr. So, for the earlier actinides, higher oxidation states are available. The maximum oxidation state observed for Ac–Pu corresponds to the number of 'outer-shell' electrons. Similar behaviour is seen in transition-metal chemistry, for example for the metals Sc–Mn in the 3d series.

From Bk onwards, the elements exhibit one common oxidation state, +3 in almost all cases, resembling the lanthanides in that respect.

Answer 4:

b) Indicate the oxidation states stable in ambient conditions.

The **large negative reduction potentials for the M^{3+}/M^{2+}** process early in the series indicate that for these metals **no aqueous chemistry of M^{2+} ions is to be expected**. The potentials become less negative with increasing atomic number, indicating increasing stability of M^{2+}, and the positive value for No is in line with No^{2+} being the most stable ion for this metal in aqueous solution

The large negative values of E^0 for M^{4+}/M^{3+} for Th and Pa indicate that **reduction to form (+3) species for these metals will be difficult**, whilst for U, Np, and Pu the smaller E^0 values indicate that both the +3 and +4 states will have reasonable stability. However, from Am onwards, Eo >2V for all these elements (except Bk), suggesting that for all these metals the (+3) state will be more favored

Add discussion of disproportionation Pu disproportionates very easily because redox potential

Question 5

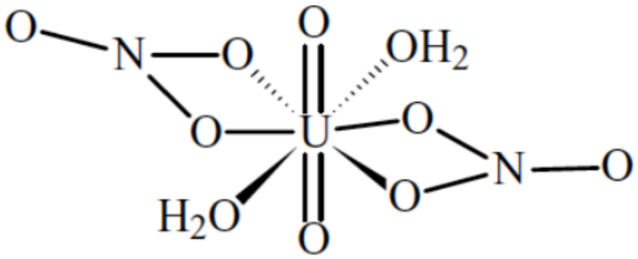
Describe common precursors of U(III), U(IV) and U(VI) and their synthesis

Answer 5

Describe common precursors of U(VI), U(IV) and U(III).

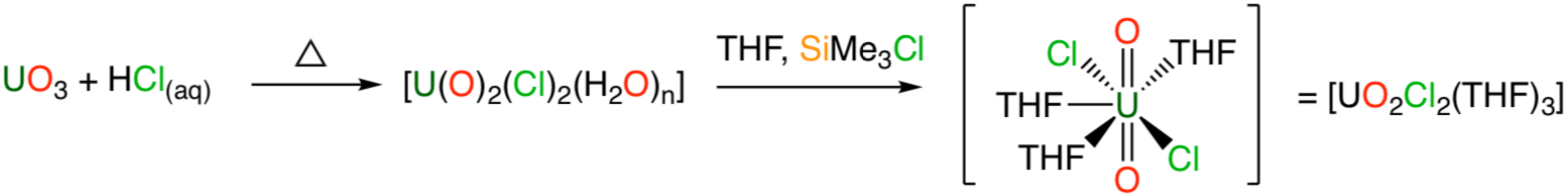
U(VI) in water

$[UO_2(NO_3)_2(H_2O)_2]$



Can form complexes with phosphine oxide. Main process in extraction

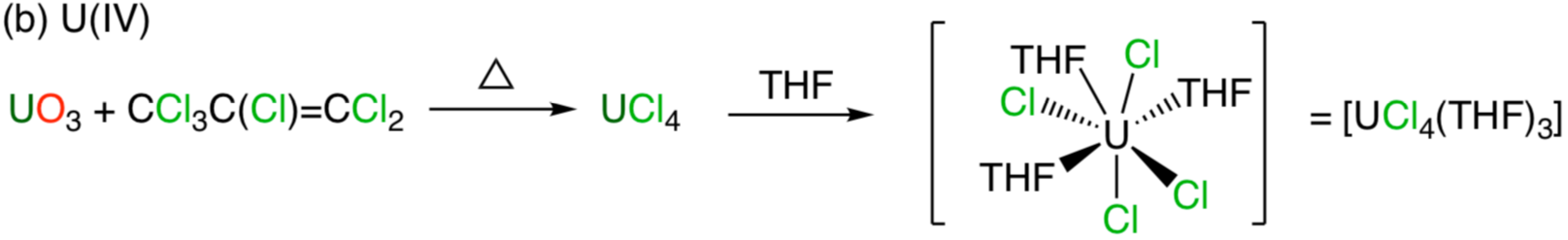
U(VI)



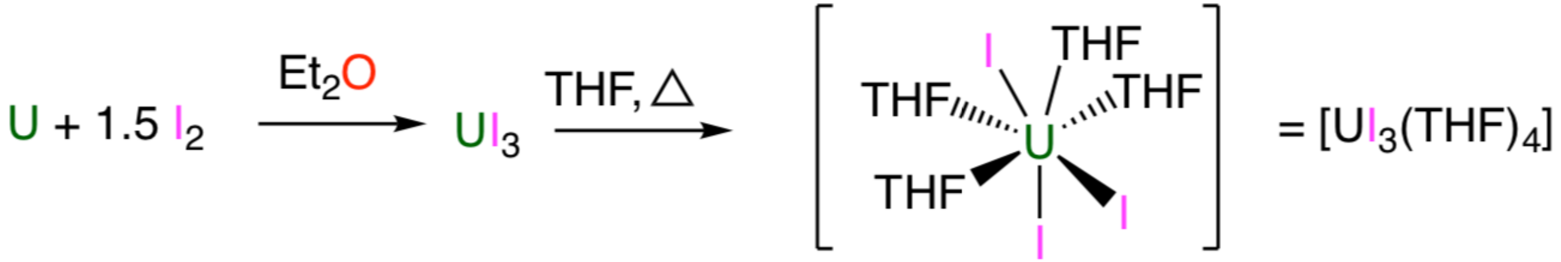
$$UO_3 + HCl_{(aq)} \xrightarrow{\Delta} [U(O)_2(Cl)_2(H_2O)_n] \xrightarrow{THF,\ SiMe_3Cl} = [UO_2Cl_2(THF)_3]$$

Answer 5

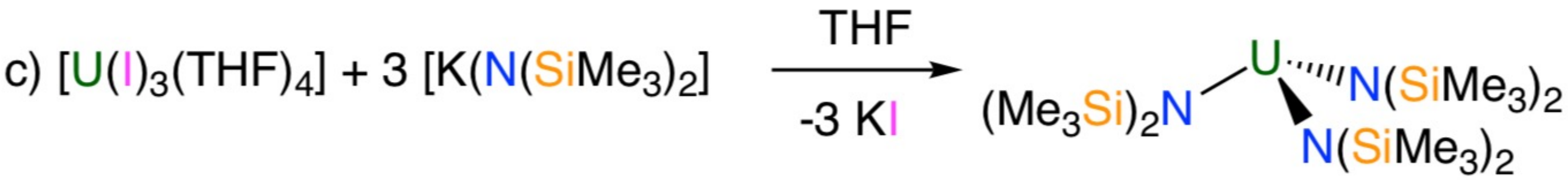
(b) U(IV)



(b) U(III)



c) U(III)



Question 6

A) **If you had to prepare a neutral siloxide U(III) complex would you choose the salt metathesis of the or the protonolysis method ? Justify.**

B) **Draw the reaction schemes to prepare the U(III) complexes using both methods.**

C) **Why tripodal ligands are particularly efficient in stabilizing highly reactive U(III) complexes ? Draw an example of such a ligand.**

Answer 6

A) If you had to prepare a neutral siloxide U(III) complex would you choose the salt metathesis of the or the protonolysis method ? Justify.

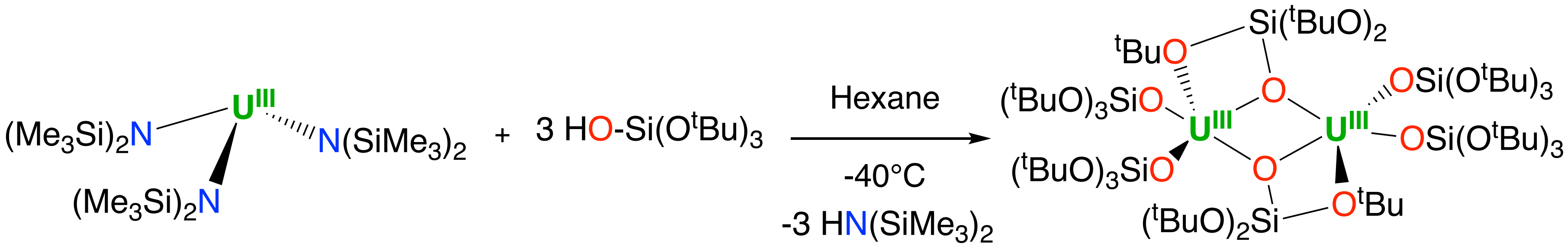
- **Protonolysis is the best method**

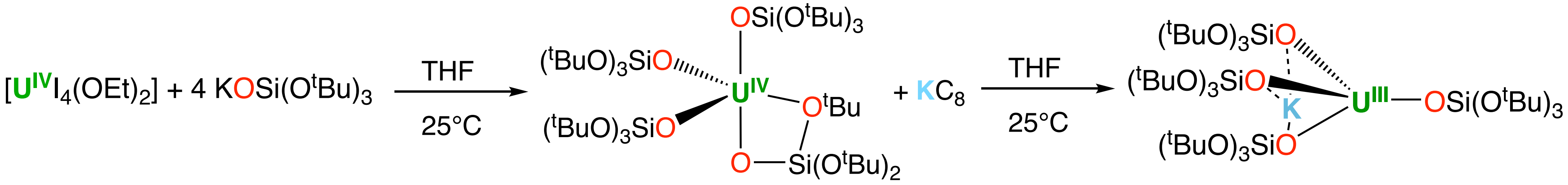
- Salt metathesis → would lead to "ate" complex

  → could lead to disproportionation to U(IV) and U(0).

Answer 6

B) Draw the reaction schemes to prepare the U(III) complexes using both method.





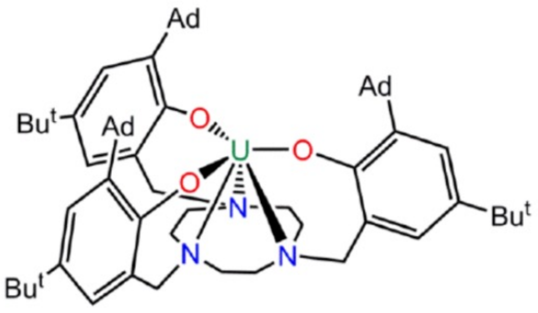
UI_3 cannot be used

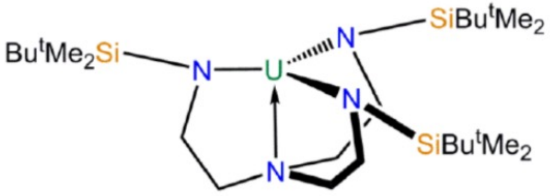
Answer 6

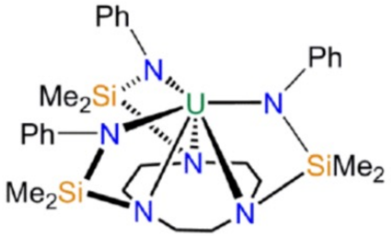
C) Why tripodal ligands are particularly efficient in stabilizing highly reactive U(III) complexes ? Draw an example of such a ligand.

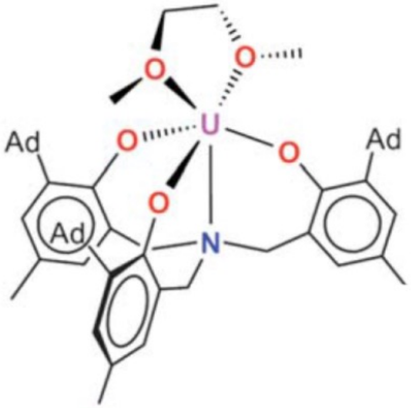
- Saturates the coordination sphere
- Kinetically protected actinides

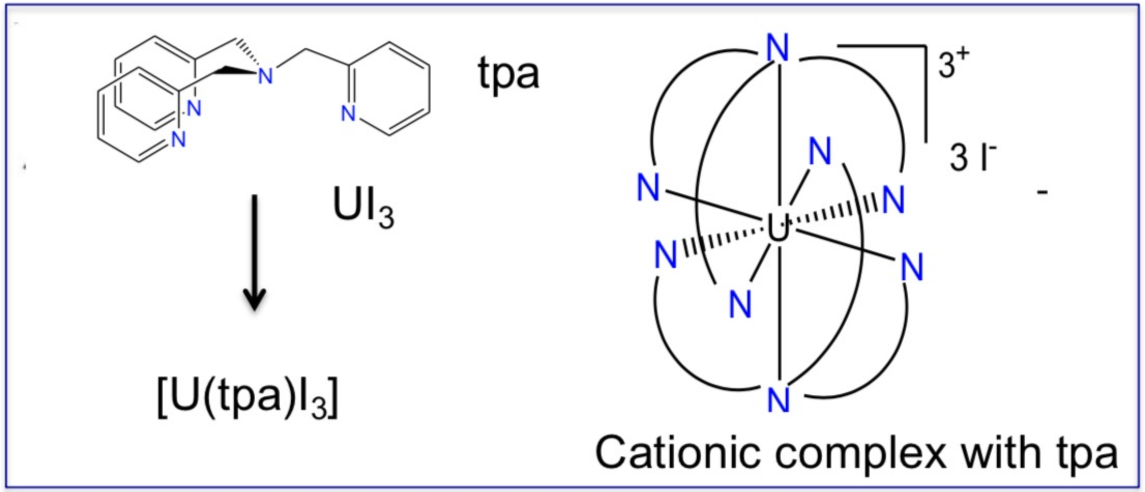
- Dative neutral atoms
- Anionic donor heteroatoms











Question 7

A) **Explain why M-L multiple bond is more common in 5f elements than 4f.**

B) **Describe common synthetic strategies to form U=O terminal bond and draw the reaction schemes.**

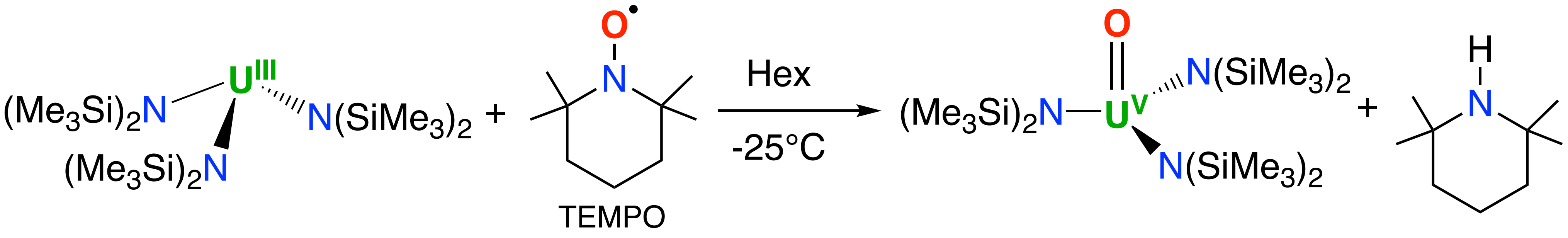
Answer 7

A) Explain why M-L multiple bond is more common in 5f elements than 4f.

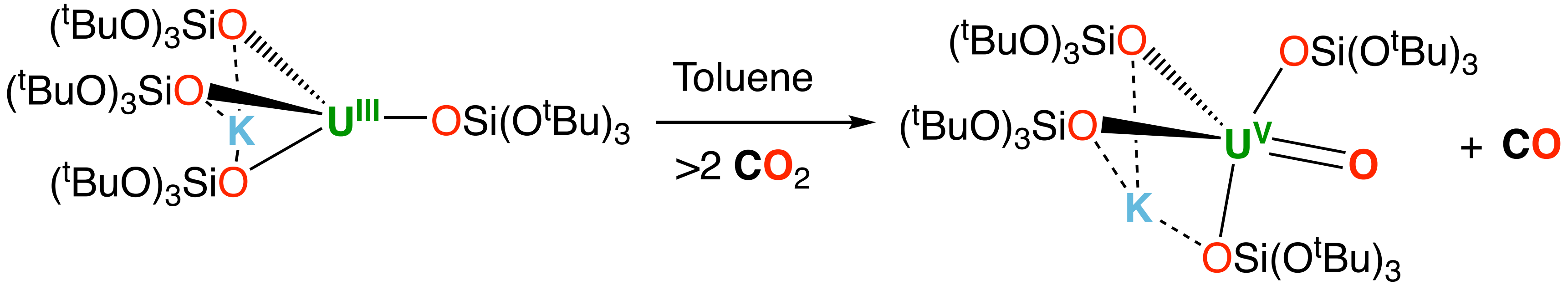
- 5f orbitals of actinides are larger and less inner orbitals respect to 4f
- their electrons interact more weakly
- 5f electrons are more chemically available.

Answer 7

B) Describe common synthetic strategies to form U=O terminal bond and draw the reaction schemes.

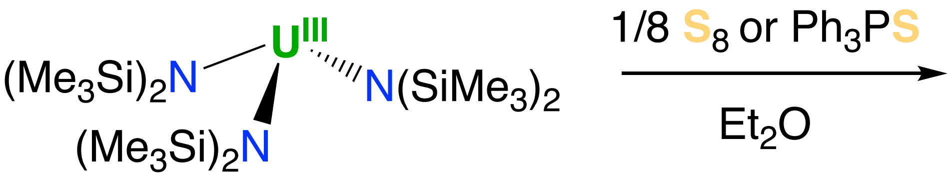


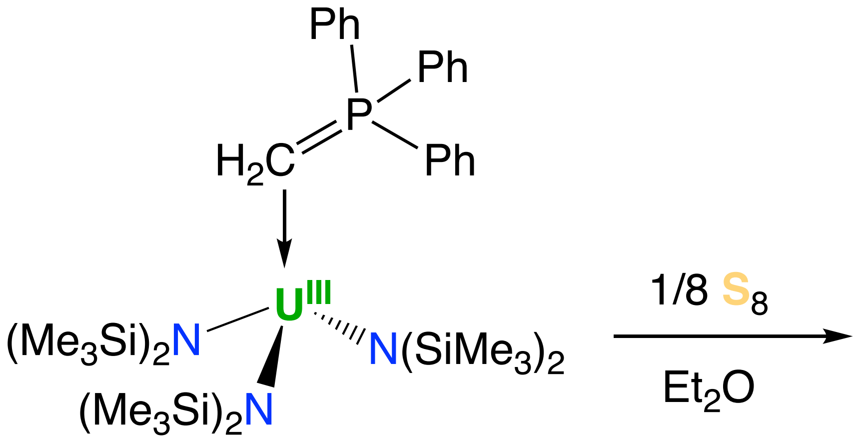
Fortier, S.; Brown, J. L.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W. *Inorg. Chem.* **2012**, 51, 1625–1633

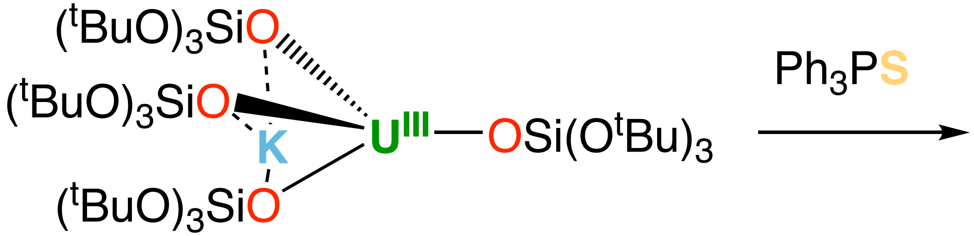


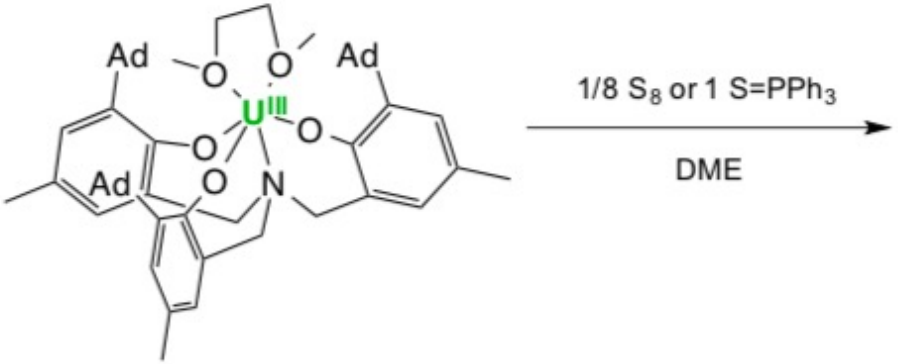
Question 8

Draw the structure of the reaction products for the following reactions and explain.



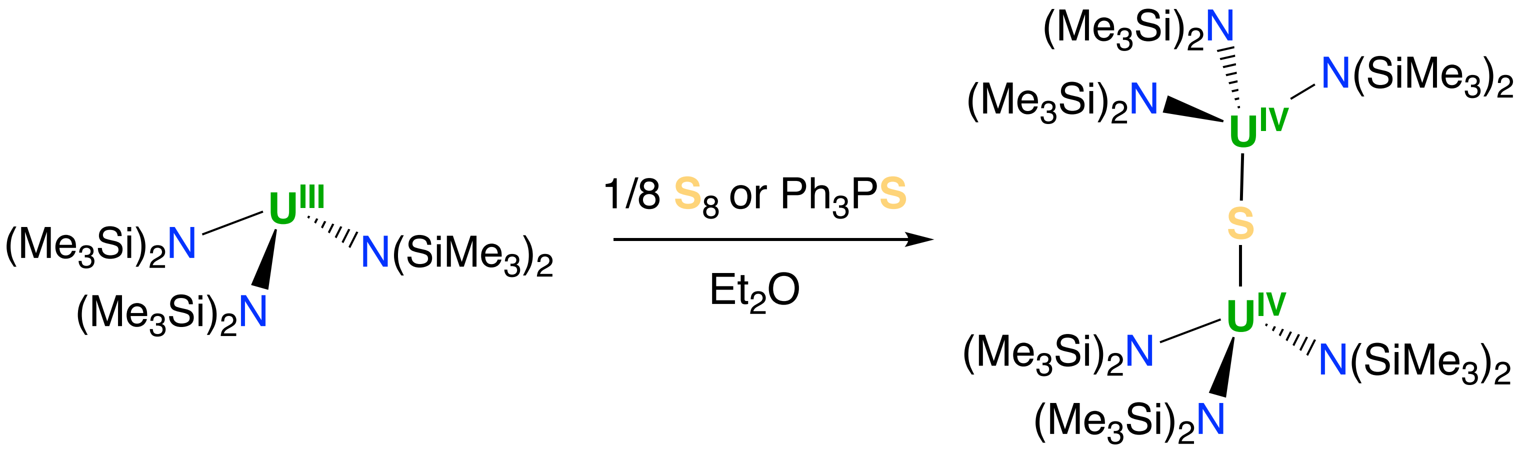






Answer 8

Draw the structure of the reaction products for the following reactions and explain.

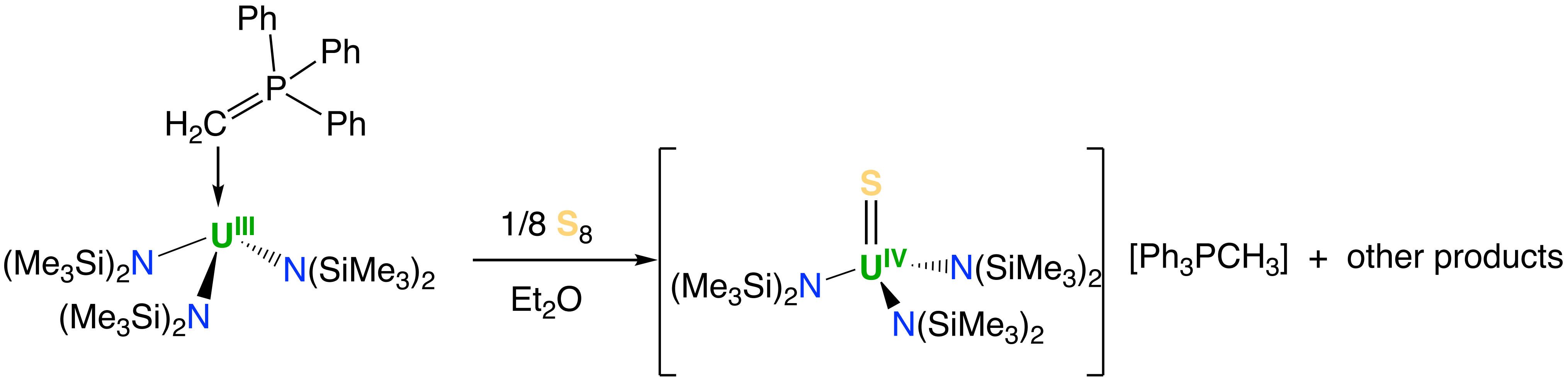


Bridging sulfide

- **S transfer reagent**
- **oxidation of 2 U(III) to U(IV)**
- **Ligand not bulky enough**
- **Open coordination sphere**

Answer 8

Draw the structure of the reaction products for the following reactions and explain.

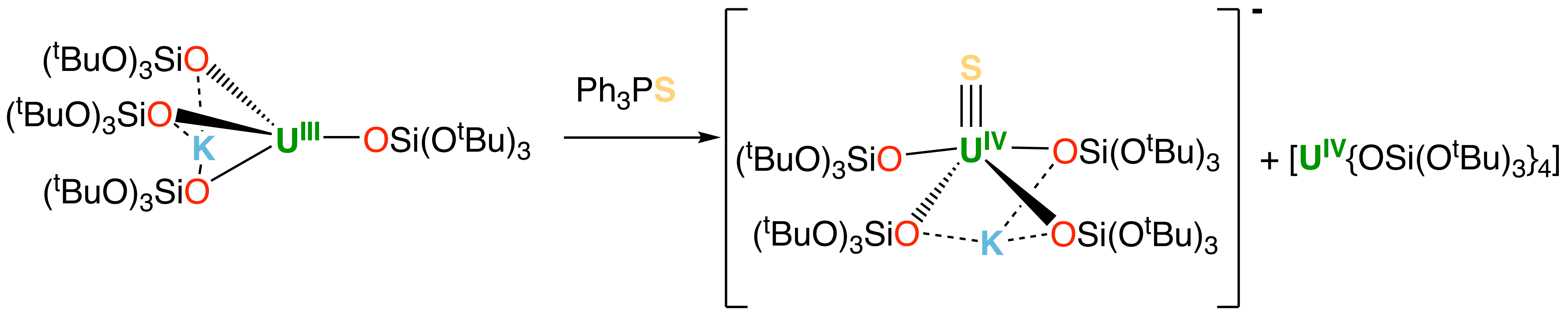


Terminal sulfide

- **S transfer reagent**
- **oxidation of U(III) to U(IV)**
- **Presence of a protecting group during S transfer**

Answer 8

Draw the structure of the reaction products for the following reactions and explain.

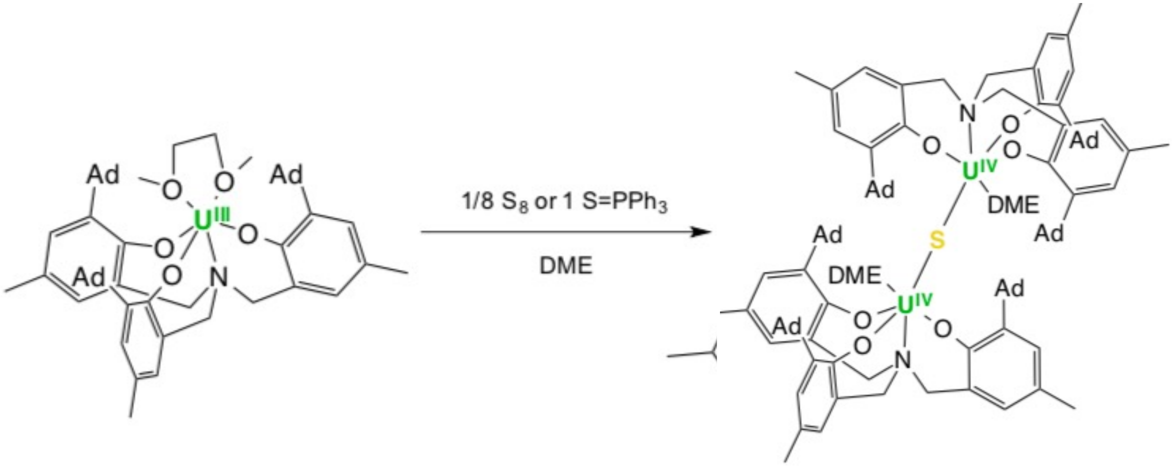


Terminal sulfide

- **S transfer reagent**
- **oxidation of 2 U(III) to U(IV)**
- **Bridging sulfide prevented by bulk of the ligand**

Answer 8

Draw the structure of the reaction products for the following reactions and explain.



Bridging sulfide

- S transfer reagent
- oxidation of 2 U(III) to U(IV)
- Tripodal ligand protects only one side of the coordination sphere