Coordination Chemistry and Reactivity of f Elements

Course 4: 4f-Coordination Chemistry

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Coordination Chemistry Group

Learning Objectives

-Recall which donor atoms and types of ligands forms stable complexes in different solvents and know why

-Know why later lanthanides form complexes with greater stability than earlier ones

-Recall the most common coordination numbers and geometries

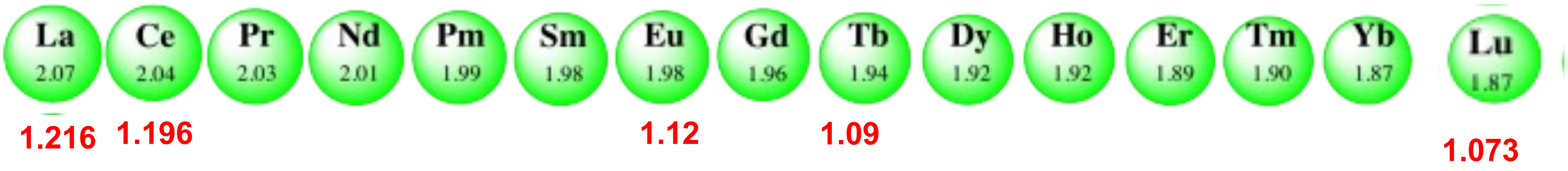
-Recognize ligands that promote low NC

-Know why lanthanides tend to form oxo and hydroxo complexes

-Recall most common synthetic strategies to Ln(III) and Ln(II) complexes formation

-Explain the limited multiple bond chemistry of the Lns.

Summary of Lanthanide Properties



- The lanthanide contraction (high difference in ionic radii (0.18 for NC of 9).
- Relatively large ionic radii : typically high coordination numbers.
- Predominantly electrostatic bonding – Hard Acids -Hard Bases.
- Similar coordination behaviour.
- Dominance of +3 oxidation state in aqueous solutions.

Unusual Oxidation States: + 2

Eu^{II} and Yb^{II} : stabilized by 4f^{7} and 4f^{14} configurations

Most developed for Sm^{II}, Eu^{II}, Yb^{II} – most stable +2 oxidation states.

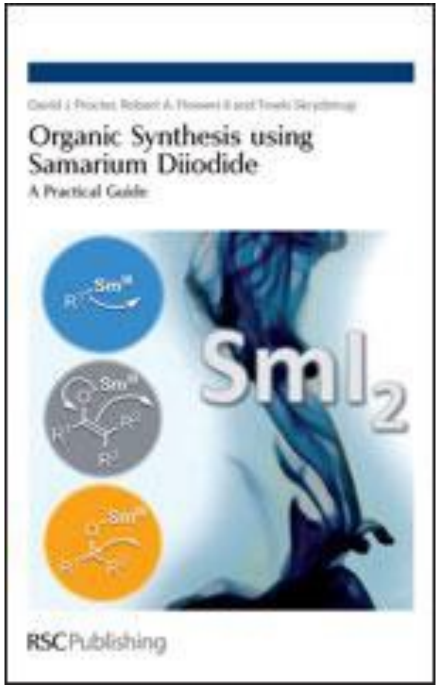
Other examples, (non-aqueous) isolable iodide complexes:
[Tm^{II}I$_2$(dme)$_3$], [Dy^{II}I$_2$(thf)$_5$], [Nd^{II}I$_2$(thf)].

[Sm^{II}I$_2$(S)$_n$] used as a powerful one electron reducing agent in organic synthesis:

E Sm^{III}/Sm^{II} = –1.55 V.

For {N(SiMe$_3$)$_2$}$^-$
[Sm{N(SiMe$_3$)$_2$}], [Yb{N(SiMe$_3$)$_2$}], [Eu{N(SiMe$_3$)$_2$}]
stable at RT.
Other "[Ln{N(SiMe$_3$)$_2$]" complexes formed *in situ*.

Alkoxides and aryloxides of Ln(II) also well developed, e.g. [Yb(OC$_6$H$_2$But$_2$-2,6-Me-4)$_2$(THF)$_2$].

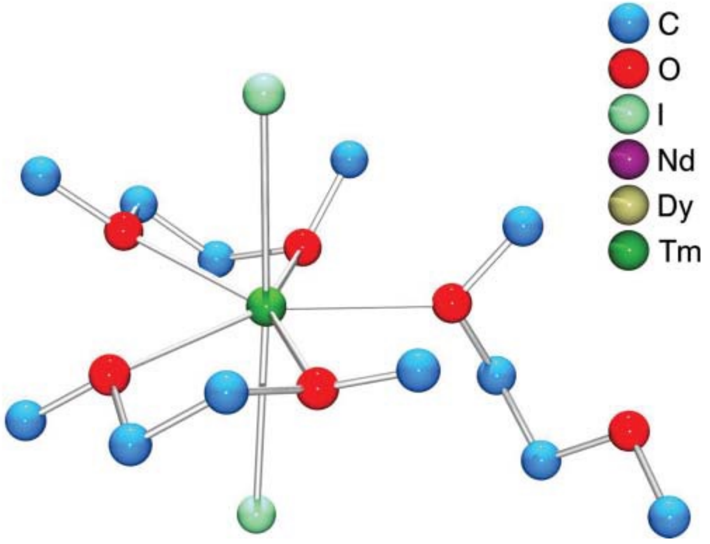


Organic Synthesis using Samarium Diiodide
A Practical Guide

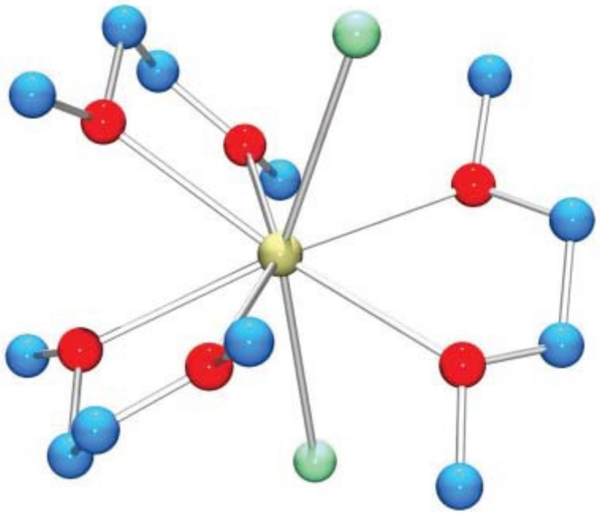
D. J. Procter,
RSC publishing, **2009**.

Complexes of Divalent Lanthanides

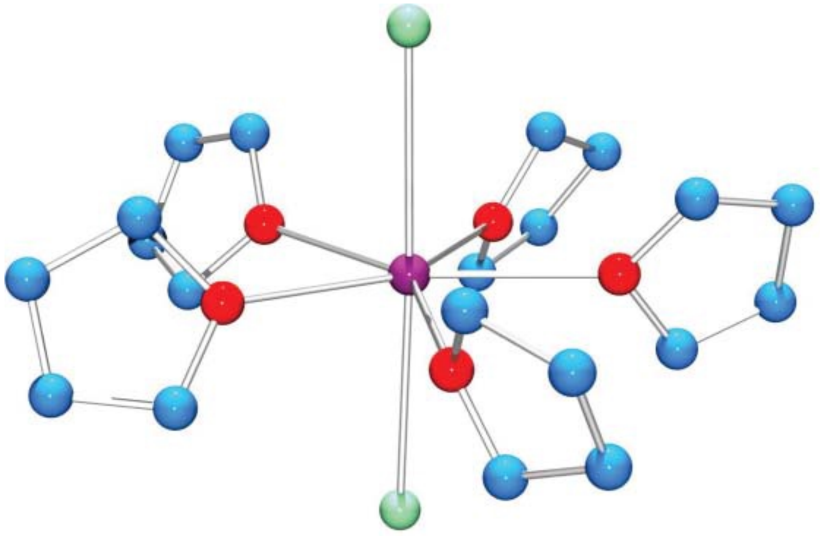
$$\mathrm{Tm} + \mathrm{I_2} \xrightarrow[\text{reflux}]{\text{DME}} \mathrm{TmI_2(DME)_3}$$



Evans, Bochkarev ACIE1997, 2001



[$DyI_2(DME)_3$]



[$NdI_2(THF)_5$] Can be isolated at -28° C

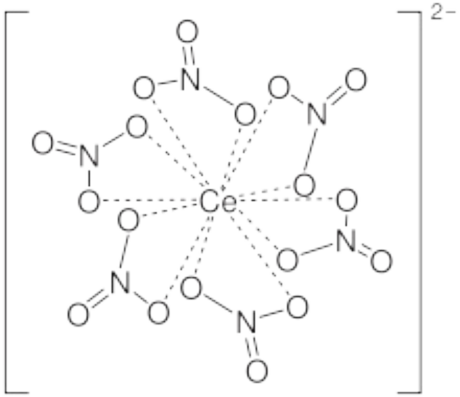
Unusual Oxidation States: + 4

Ce^{IV} was the only Ln with stable +4 O. S until 2019.

Pr^{IV} and Tb^{IV} first molecular complexes isolated in 2019 and 2020

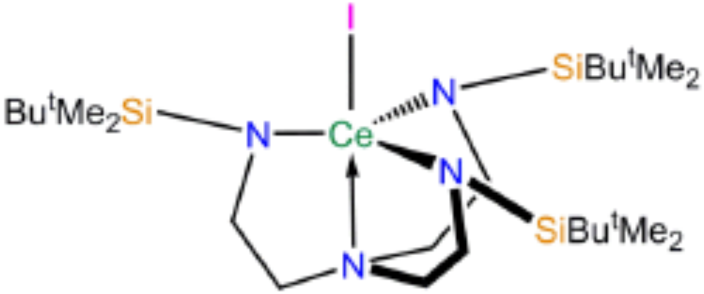
Ce^{IV} can be stable in aqueous solution, but is a strong oxidant

Ceric Ammonium Nitrate , CAN
$[Ce(NO_3)_6](NH_4)_2$ An oxidant stable in aqueous conditions used in organic synthesis (alcohols, phenols, and ethers)



Ce(IV) is stabilized by hard ligands such as alkoxides and amides

For example $[Ce(acac)_4]$
$[Ce(OR)_4(THF)_2]$ (R= But, SiPh3)



Geometries and Coordination Numbers(NC)

Bonding is predominantly electrostatic: CN and geometry determined by Ln^{III} radius and ligand size.

1) No directional component to bonding. So geometry essentially determined by ligand steric factors rather than crystal field (d-block case)

2) The coordination number is maximised to that allowed by sterics and until the charge of Ln(III) is « neutralized ». So a wide range of NC form 2 to 12 is possible because they are larger than transition metals (La^{3+} 1.032 Å and Lu^{3+} 0.861 Å, Ti^{3+} 0.670 Å)

More common 6-12

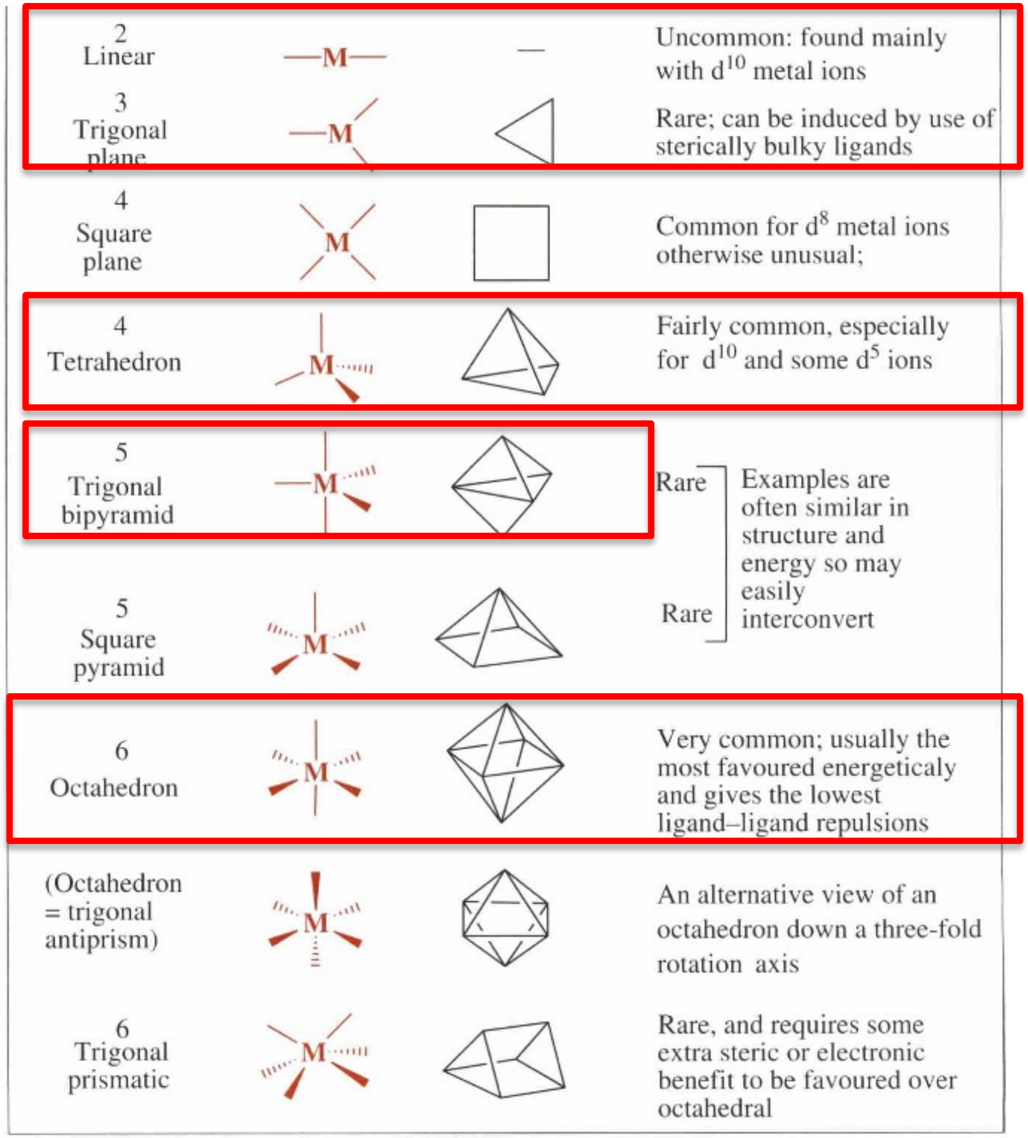
For example for H_2O ligands, $[Ln(H_2O)_n]^{3+}$:

n = 9 for La^{III}-Eu^{III}; n = 8 for Gd^{III}-Lu^{III}.
The switch from CN9 to CN8 at Gd^{III} often observed: The **gadolinium break**.

NB these are dynamic environments. Mean coordinated H_2Os in solution may be non-integer, e.g. Sm^{3+}(aq) n ~ 8.5.

Coordination geometries: d block versus f block

For lanthanides: only geometry leading to minimized repulsion will be found.
Usually more distorded than d-block



2 Linear		Uncommon: found mainly with d^{10} metal ions
3 Trigonal plane		Rare; can be induced by use of sterically bulky ligands
4 Square plane		Common for d^8 metal ions otherwise unusual;
4 Tetrahedron		Fairly common, especially for d^{10} and some d^5 ions
5 Trigonal bipyramid	Rare	Examples are often similar in structure and energy so may easily interconvert
5 Square pyramid	Rare	
6 Octahedron		Very common; usually the most favoured energeticaly and gives the lowest ligand–ligand repulsions
(Octahedron = trigonal antiprism)		An alternative view of an octahedron down a three-fold rotation axis
6 Trigonal prismatic		Rare, and requires some extra steric or electronic benefit to be favoured over octahedral

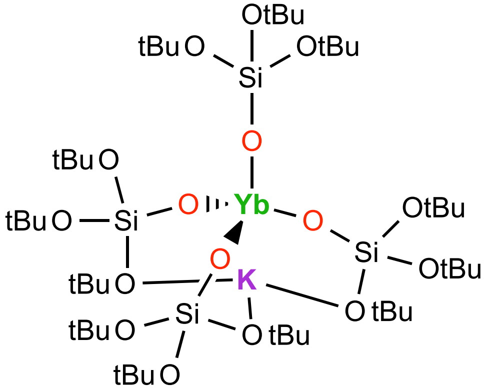
Found with bulky ligands as $(N(SiMe)_3)^-$

Low Coordination Numbers (CN)

Low coordination number stabilized with bulky ligands

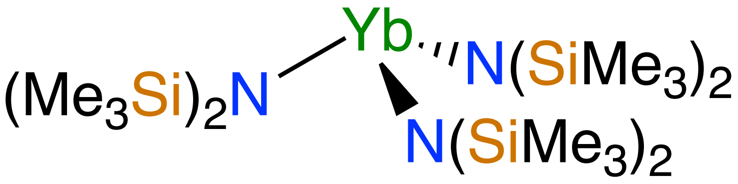
CN: 4 (e.g. $[\mathrm{Yb}^{III}(\mathrm{OSi}(\mathrm{OtBu})_3)\mathrm{K}])$

Siloxides



Angew. Chem. Int. **2014**, 53, 10448

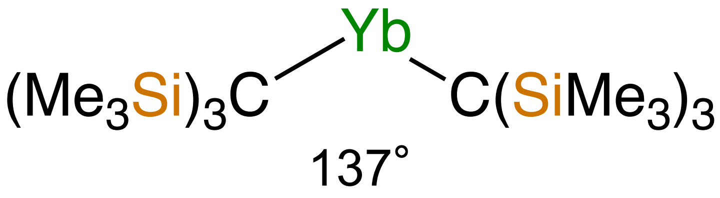
CN: 3 (e.g. $[\mathrm{Yb}^{III}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}_3])$



Alkyl and alkyl-amides

Coord. *Chem*. *Rev*., **1977**, *24*, 1

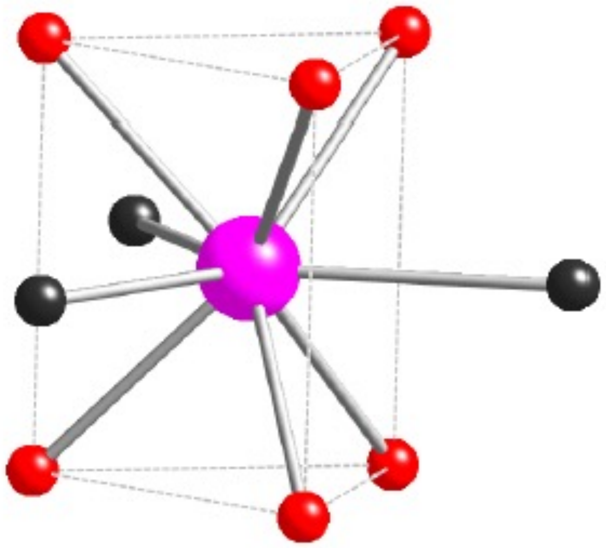
CN: 2 (e.g. $[\mathrm{Yb}^{III}\{\mathrm{C}(\mathrm{SiMe}_3)_3\}_2])$



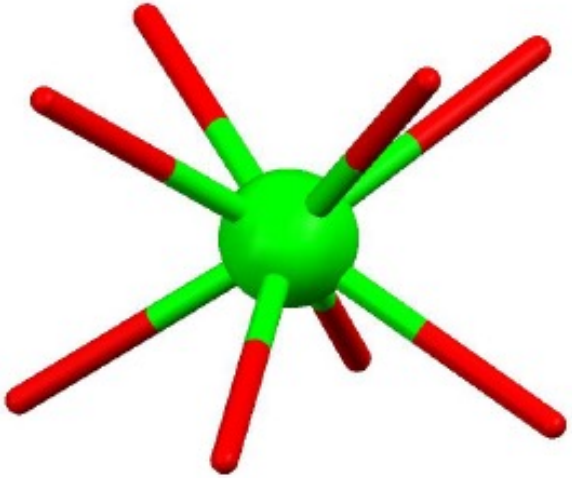
Bent due to agostic Yb---C interactions

J. *Am*. *Chem*. *Soc*., **1994**, *116*, 12071

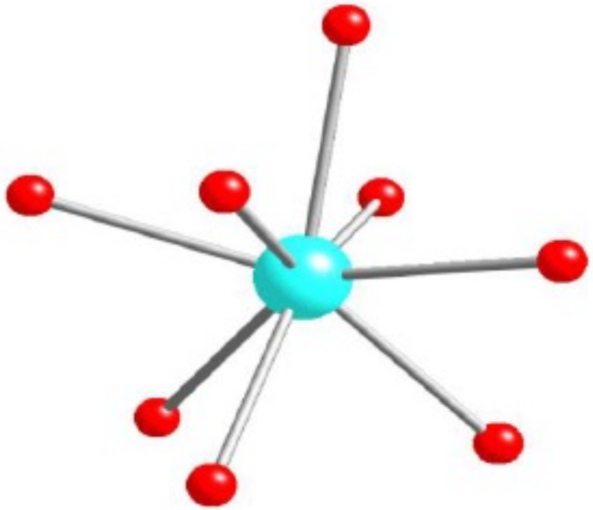
Most Common Geometries for Coordination Numbers(NC) 8 and 9



Tricapped trigonal
Prism
CN 9



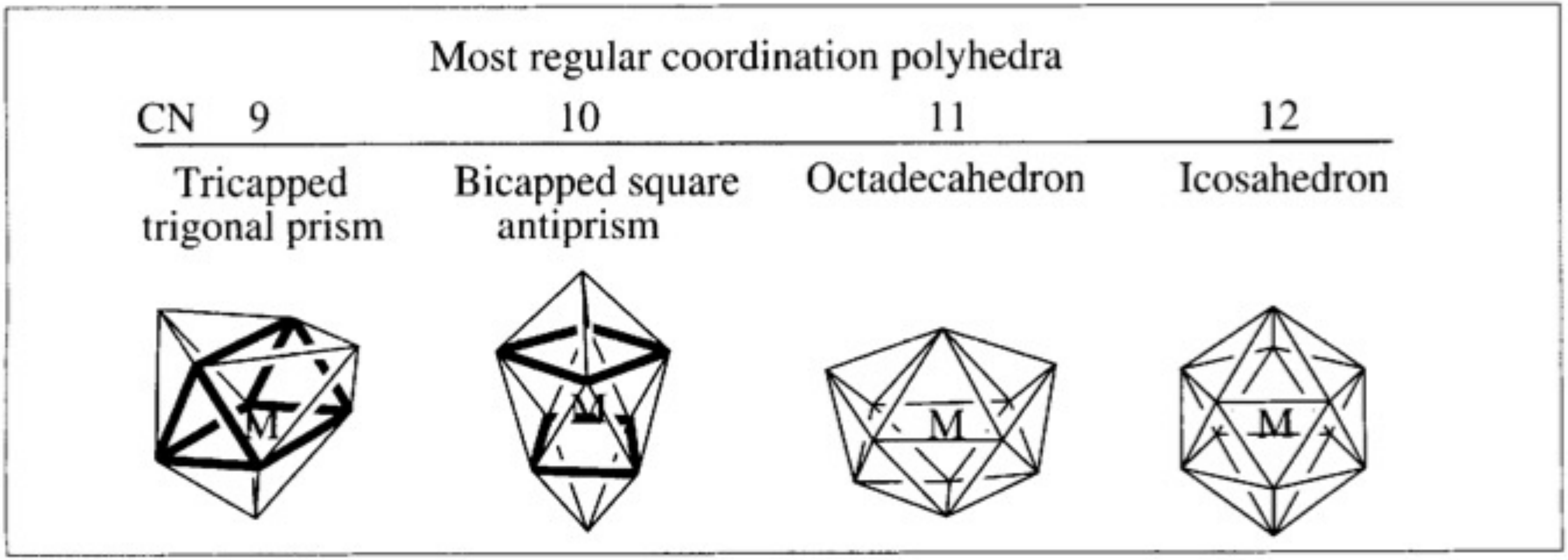
Square anti-prism
CN 8



Dodecahedron
CN 8

Lanthanides generally are large ions therefore high coordination numbers are common with small ligands such as Cl^- and polydentate ligands (up to 12)

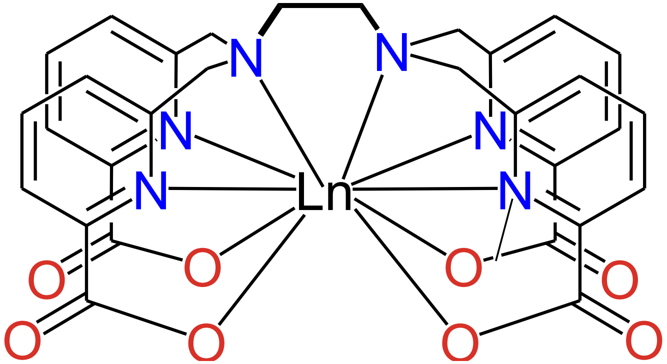
10-12 Coordination numbers can be found with polydentate ligands



Most regular coordination polyhedra

CN	9	10	11	12
	Tricapped trigonal prism	Bicapped square antiprism	Octadecahedron	Icosahedron

Regular geometry are only found with identical ligands ($[La(NO_3)_6]^{3-}$



In the case of polydentate ligands
Polyhedra are distorded

Complexes Stability

The crystal field of coordinated ligands does not remove the degeneracy of the 4f orbitals.

As there is no Crystal Field Stabilisation Energy, low barriers to ligand substitution. Therefore these complexes are often **kinetically labile**.

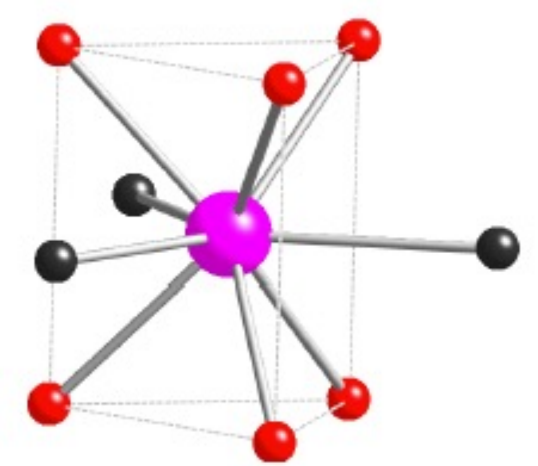
As in TMs multidentate ligands often displace monodentate ligands by chelate/macrocyclic effects:

Thermodynamic stability is proportional to the sum of pKas and preorganisation

High stability in water (as required by biomedical applications is achieved with

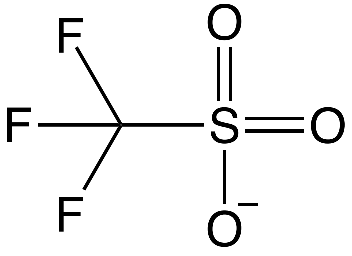
- Polydentate ligands with negative O, N donors
  aminocarboxylate ligands , aminophenolate etcc
- In organic media the competition with solvents is less important
  But there is still competition with anions
  Stable complexes can be formed with polydentate ligands with neutral N, O donors

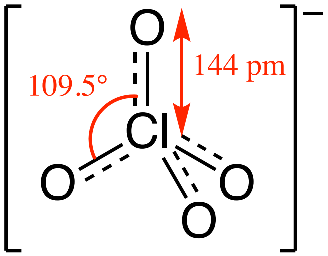
Hydrated Salts



Crystallisation of aqua ions in the presence of weakly Coordinating anions: triflate, perchlorate
Trigonal prismatic $[Ln(H_2O)_9]X_3$ complexes are formed for early lanthanides (La-Eu)
Square antiprismatic $[Ln(H_2O)_8]X_3$ for late lanthanides

Water molecules are substituted by coordinating anionic ligands in water



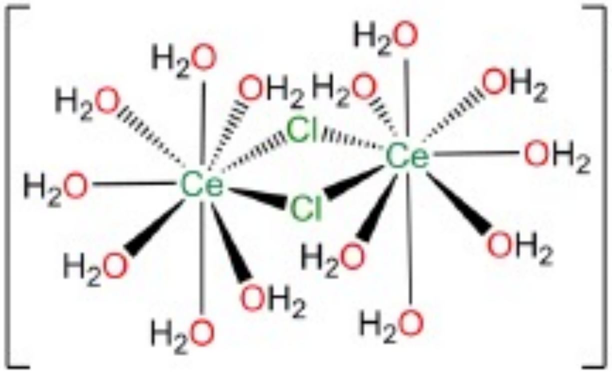


triflate perchlorate

Ln salts of coordinating anions in water

Nitrates – $[Ln(NO_3)_3(H_2O)_5]$ (Ln = La, Ce) CN 11.
$[Ln(NO_3)_3(H_2O)_4]$ (Ln = Pr-Yb) CN 10.

$CeCl_3 + xsH_2O \rightarrow 0.5\ [Ce(H_2O)_6\}(\mu\text{-}Cl)]_2[Cl]_4$ CN9



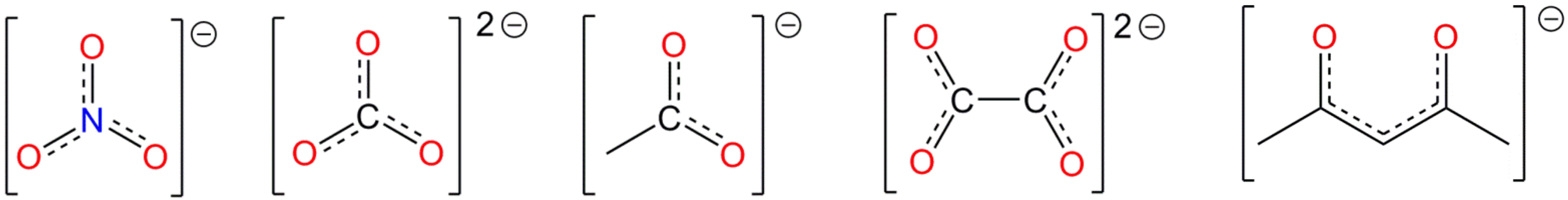
4+

$4Cl^-$

Neutral ligands will not displace chloride or nitrates

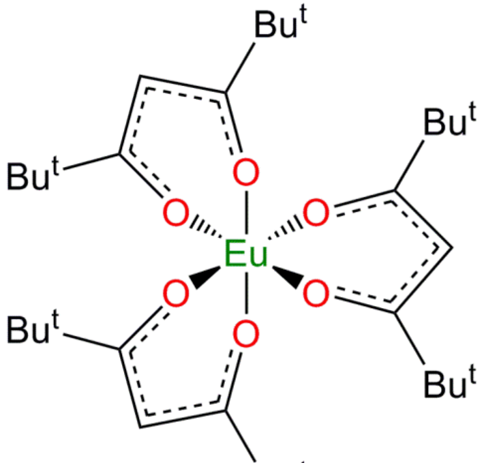
Anionic Bidentate Negative O-donors

Simple O-donor ligands ubiquitous in classic lanthanide coordination chemistry



acac

e.g. nitrates, carbonates, acetates, oxalates,
β-diketonates, e.g. acetylacetonate, acac .



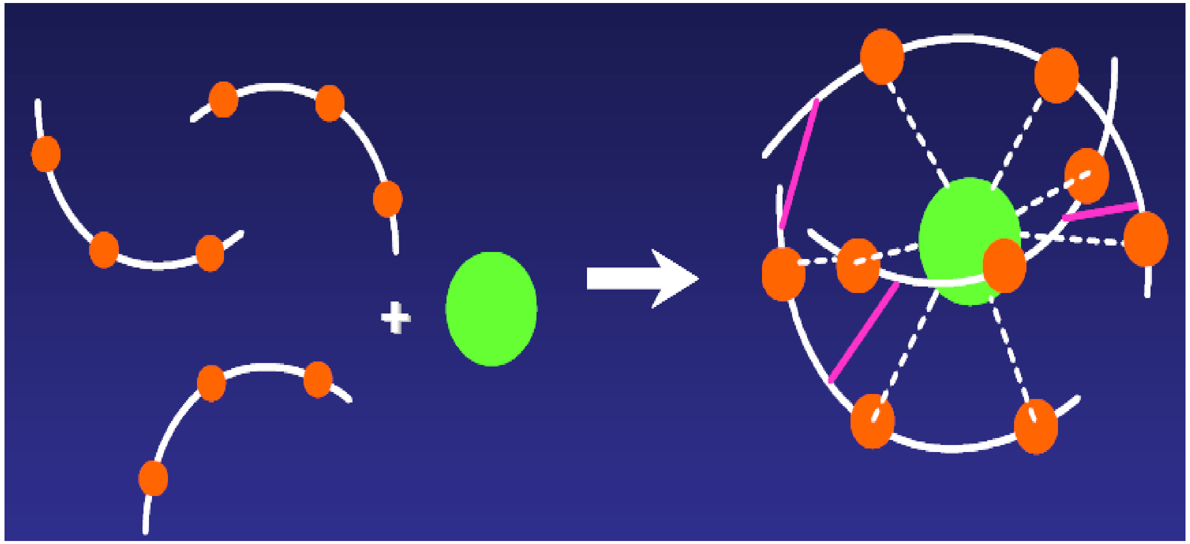
$[Eu(dpm)_3]$

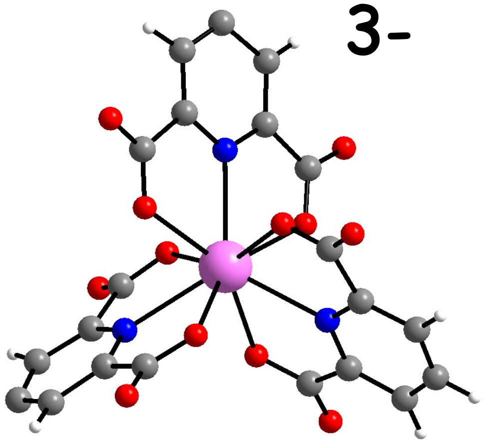
$LnX_3 + 3\,[Na(acac)] \rightarrow [Ln(acac)_3(H_2O)_2] + 3\,NaX$

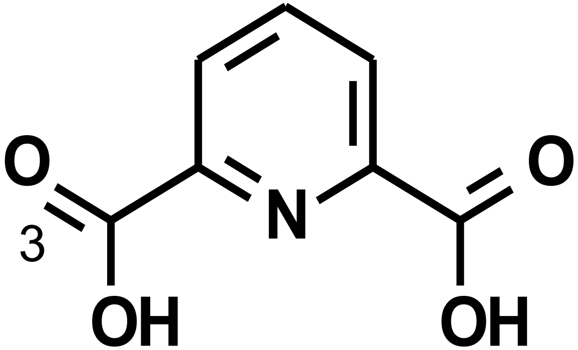
Anionic Tridentate O-donors

Self-assembly process leads to nonadentate complexes

Partial dissociation in water



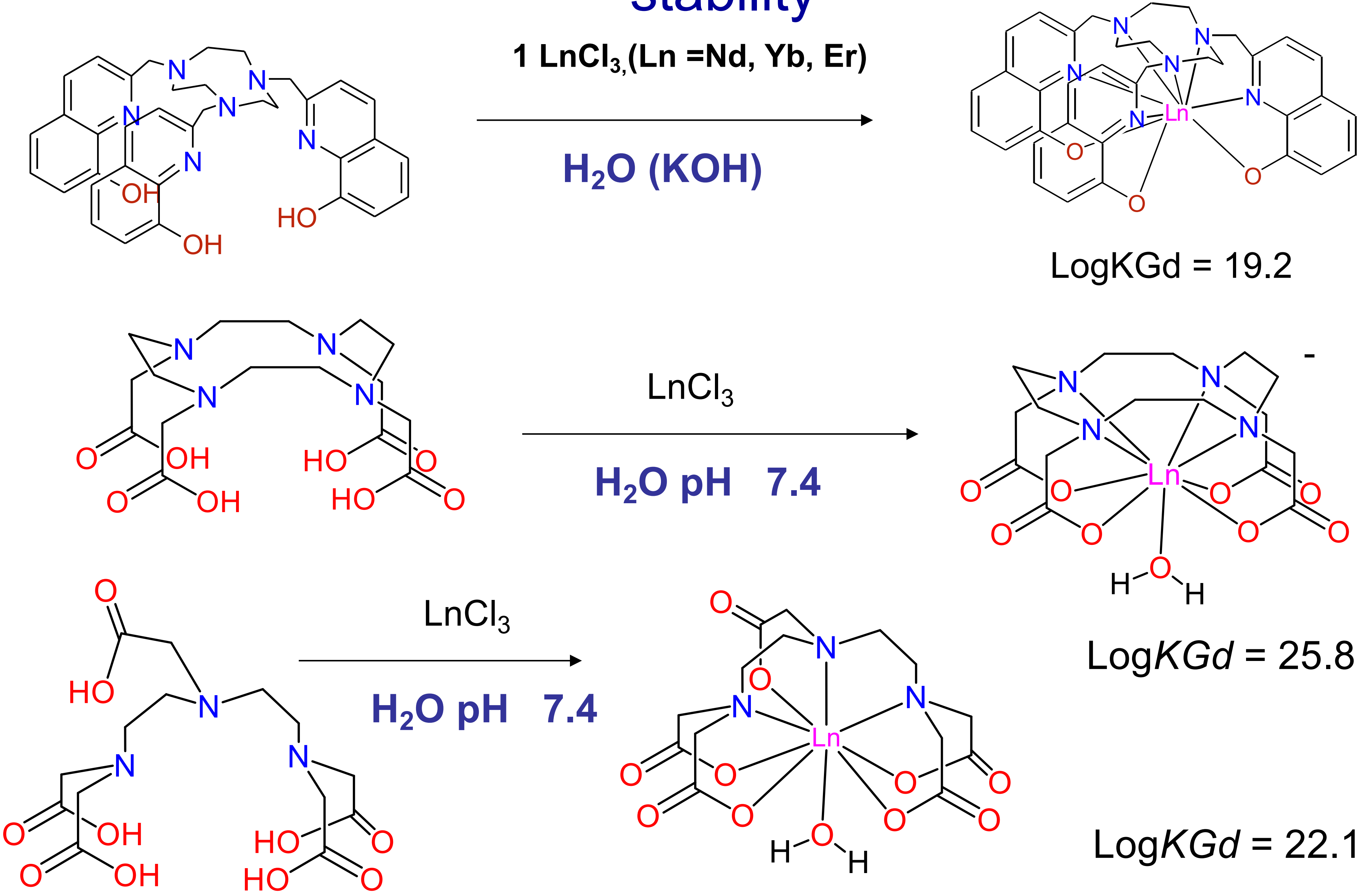




$$\xrightarrow[\text{KOH} \quad -6H^+]{[Ln(H_2O)_9]^{3+}} \quad [Ln(dpa)_3]K_3 \; + [Ln(dpa)_2(H_2O)_3]^-$$

LogK_i = 8.7, 8.1, and 5.6 (i = 1-3)

Anionic Multidentate N,O-donors: Thermodynamic stability



1 $LnCl_3$,(Ln =Nd, Yb, Er)

H_2O (KOH)

LogKGd = 19.2

$LnCl_3$

H_2O pH 7.4

-

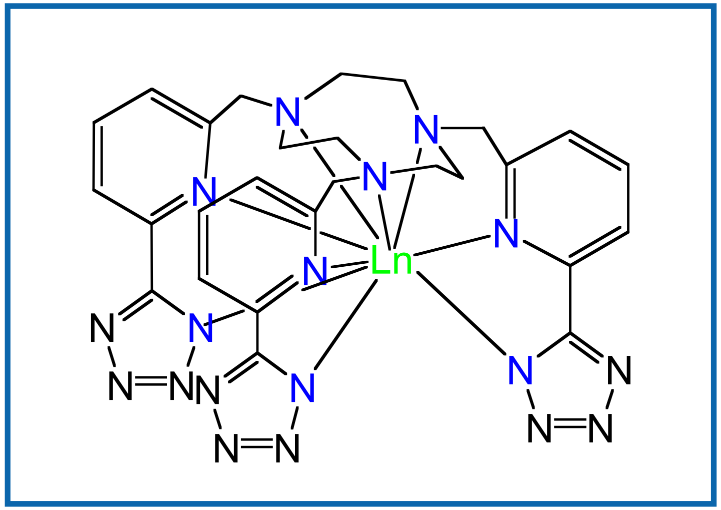
Log*KGd* = 25.8

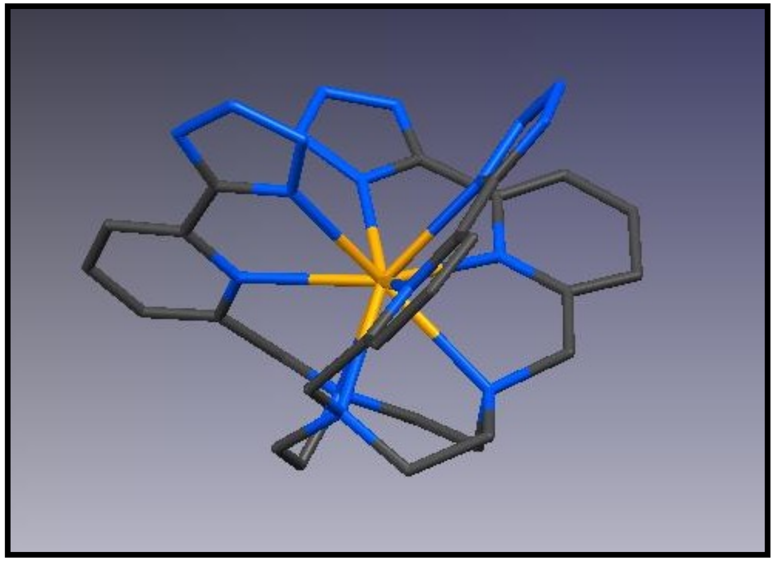
$LnCl_3$

H_2O pH 7.4

Log*KGd* = 22.1

Anionic multidentate N-Donors





tetrazole

* is analogous of carboxylate
(pKa of tetrazole = 4.8-4.9)

Ln = Nd, Eu, Gd, Tb,Yb

A isostructural series

Inorg. Chem, **2008**, 47 (10), 3952

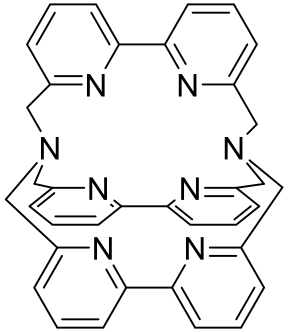
Water Stable Neutral Multidentate N/O-donors

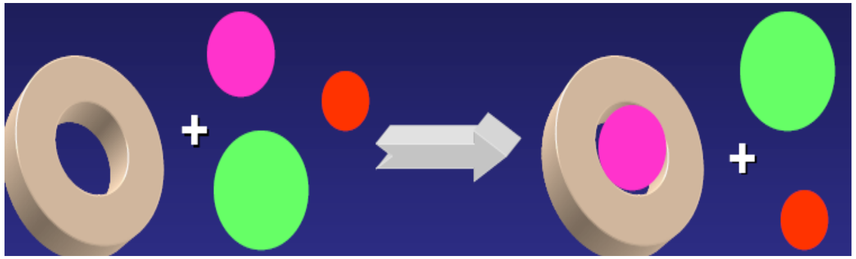
Kinetic Stability

Rigid Receptors

Macrocyclic effect

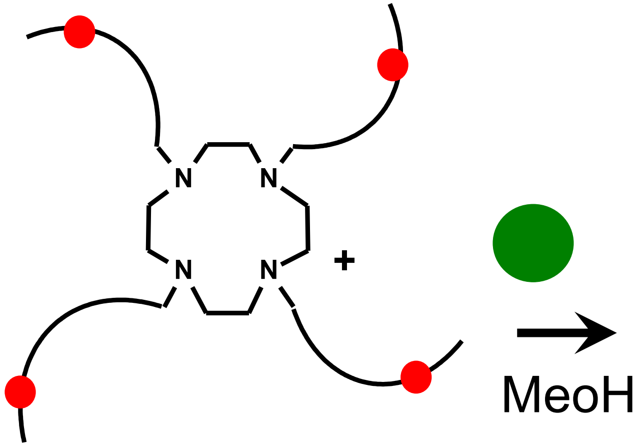
Cryptands,



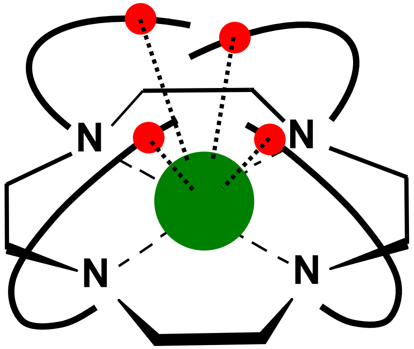


podands

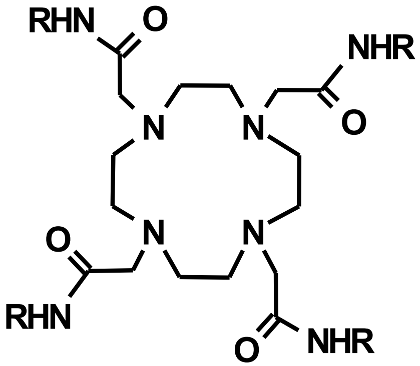
Macrocyclic amides



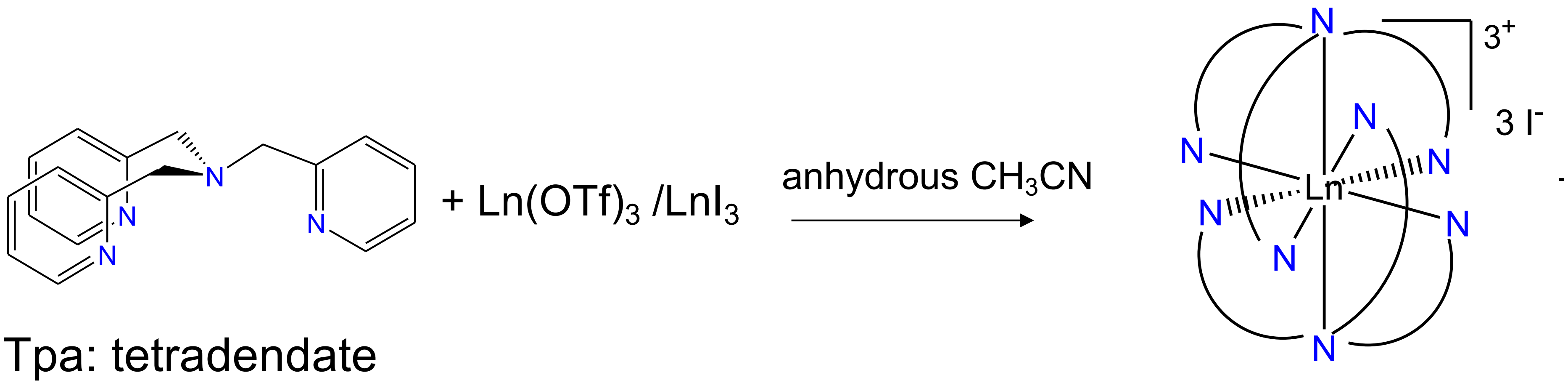
MeoH



Induced Cavity



Ln(III) Complexes of Neutral N-donor Ligands

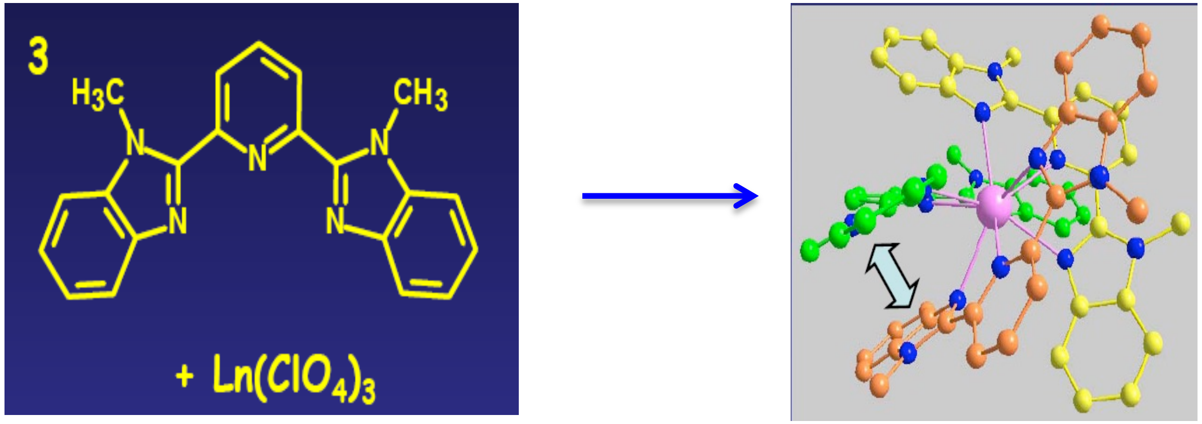


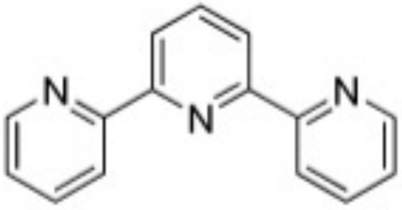
Tpa: tetradentate

L. Natrajan *et al.*,Inorg. Chem., 2005, 4756.

Ce(tpa)$_2$I$_3$

Tridentate ligands





terpy

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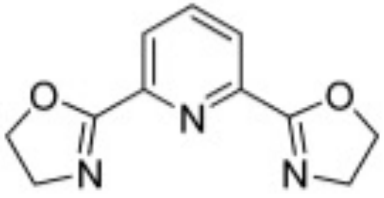


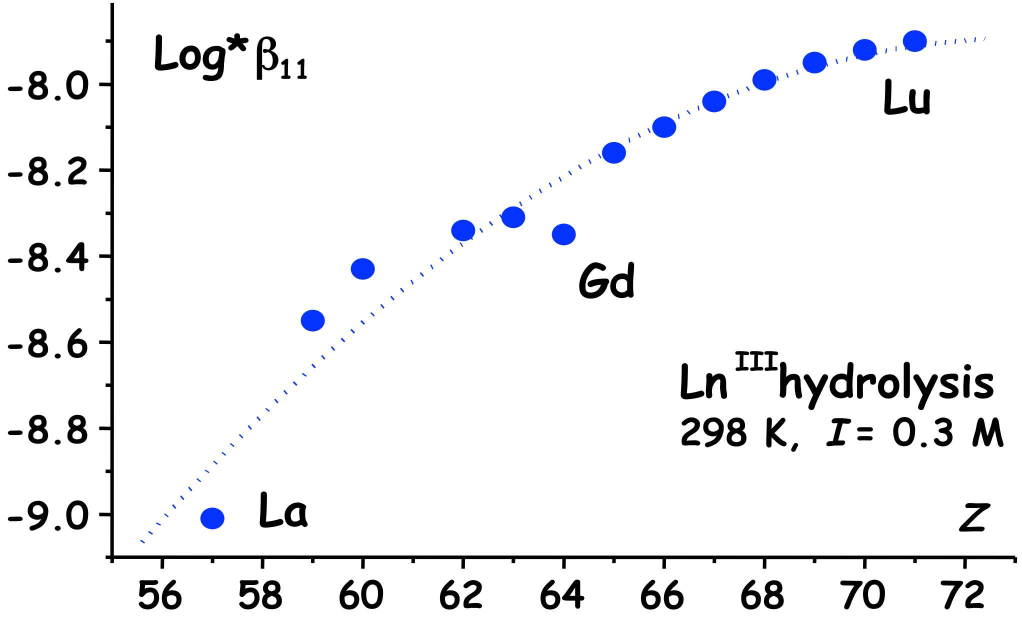
pybox

Stable in anhydrous conditions

Hydrolysis

$$m\,[\mathrm{Ln(H_2O)_x}]^{3+} \leftrightarrows [\mathrm{Ln_m(OH)_\ell(H_2O)_{(n-\ell)}}]^{(3m-\ell)+} + \ell\,\mathrm{H^+}$$

$$^{*}\beta_{\ell,m} = \frac{[\mathrm{Ln_m(OH)_\ell\,(H_2O)_{(n-\ell\,)}}\,]^{(3m-\ell)+}[\mathrm{H^+}]^{\ell}}{[\mathrm{Ln(H_2O)_n}^{3+}]^{m}}$$



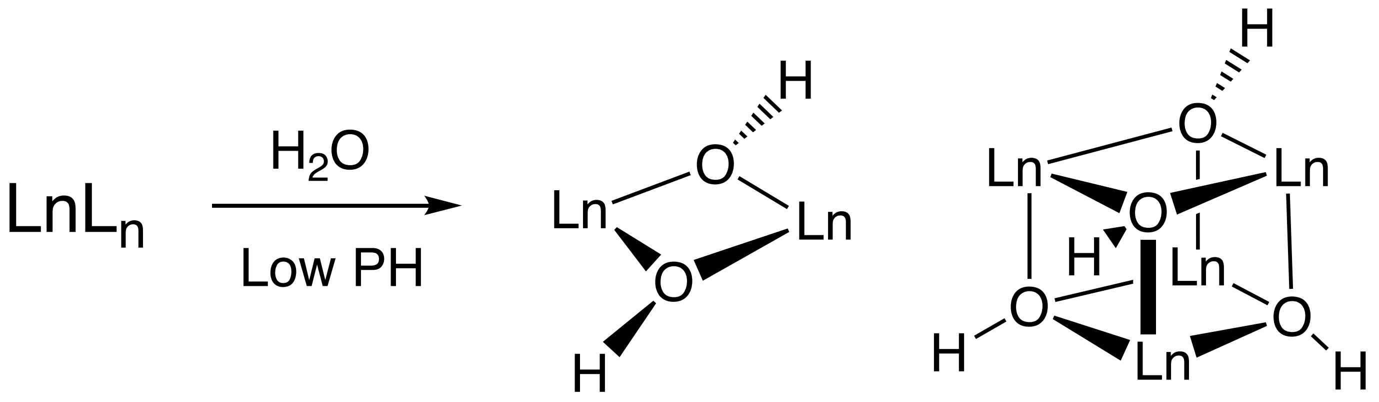
Ligand binding will limit hydrolysis depending on stability constant

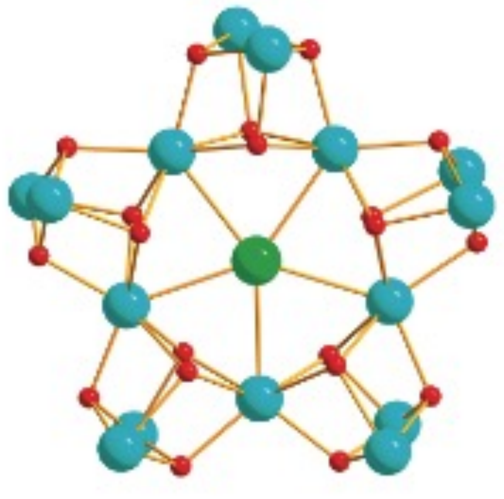
Example Ligand L, LogK_1 = 3, pH = 7, Log*β_{11} = -8 $[\mathrm{L}]_{\mathrm{free}} = 10^{-3}$ M
$[\mathrm{LnL}] : [\mathrm{LnOH}] : [\mathrm{Ln_{aq}}]$ = 45 : 45 : 10 %

Hydrolysis: a route to polymetallic complexes

Lanthanides form polymeric hydroxides at high pH but in the presence of ligands clusters can be formed by controlled hydrolysis of lanthanides in water

Interesting for artificial nucleases for the hydrolytic cleavage of DNA and RNA, magnetic properties, fixation media for atmospheric CO_2 , molecular magnetic material



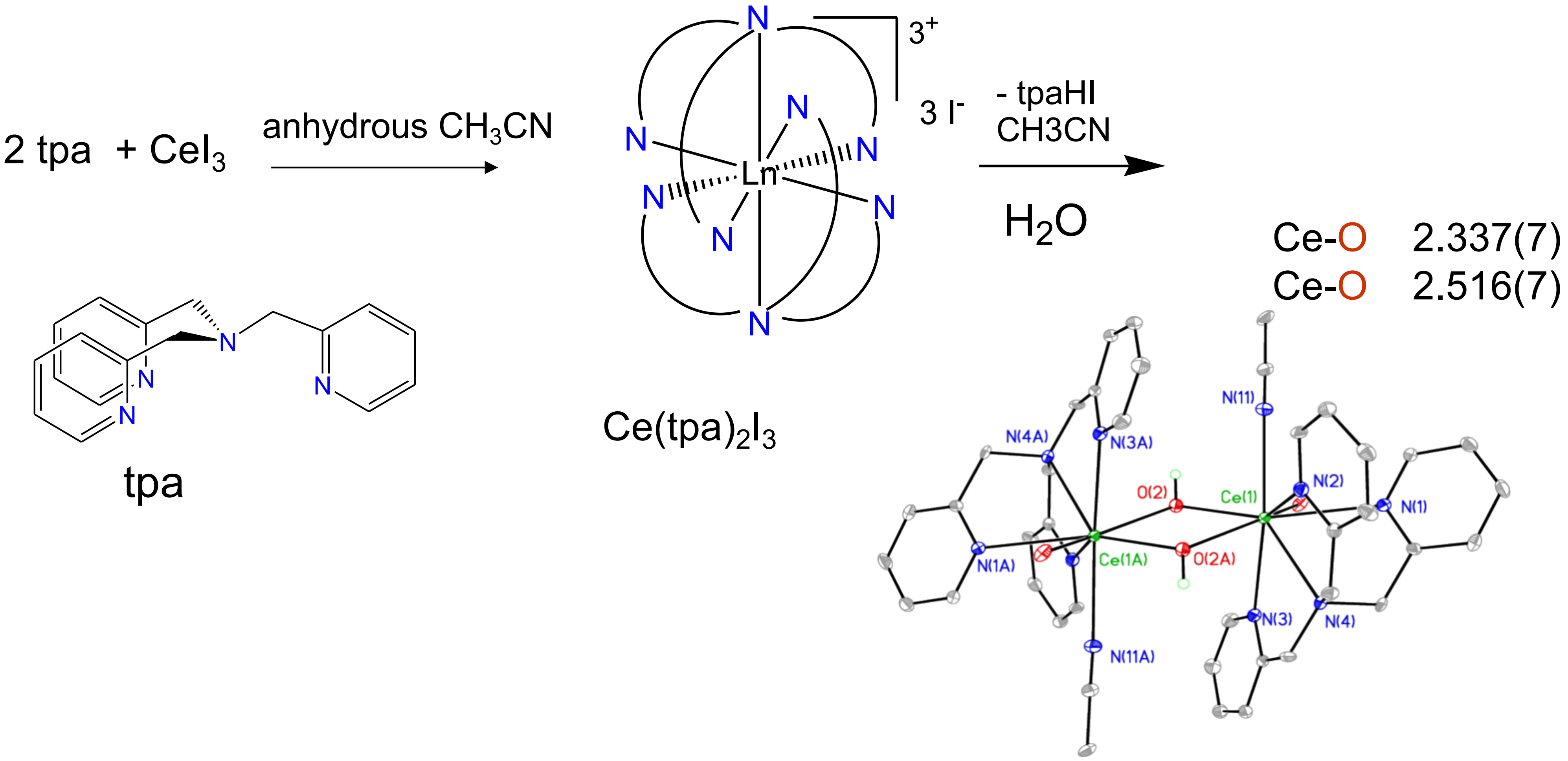


L = Tyrosine , importance of the halide anion in the assembly of 4 $[Eu_4(\mu_3OH)_4]$ cubanes

Species only isolated in the solid state
J. AM. CHEM. SOC. 2009, *131*, 6918–6919

Hydrolysis of Ln(III) Complexes in Anhydrous Solvents

Under Ar and in the presence of water, $Ln(tpa)_2X_3$ ($X = I^-$, OTf^-), undergo controlled hydrolysis to form dinuclear Ln(III) Hydroxo complexes:



$2\ tpa + CeI_3 \xrightarrow{\text{anhydrous } CH_3CN}$

tpa

$Ce(tpa)_2I_3$

$\xrightarrow[H_2O]{-\ tpaHI,\ CH3CN}$

Ce-O	2.337(7)
Ce-O	2.516(7)

L. Natrajan *et al.*,Inorg. Chem., 2005, 4756.

$[Ce(tpa)(\mu_2\text{-}OH)(MeCN)(H_2O)]_2I_4$

Non-Aqueous Coordination Chemistry

Complexes with Ln–E bonds (E = N, P, S etc.) are often highly air- and moisture sensitive and are readily cleaved by protic solvents.

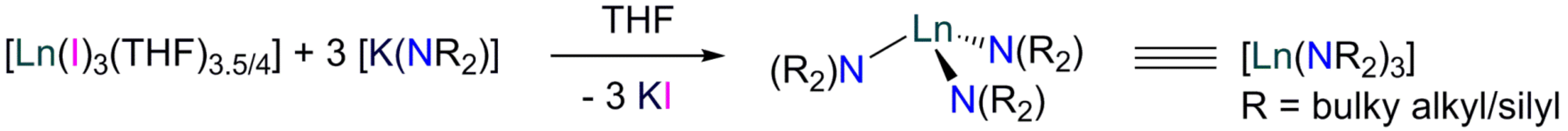
(Relatively stable complexes are those of polydentate aromatic N-donor ligands)

$[La(NO_3)_3]$ + bipy/phen → $[La(NO_3)_3(\text{bipy/phen})_2]$

Many catalytic applications.

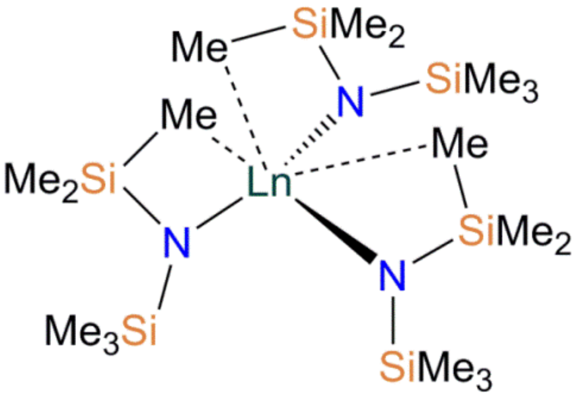
Most common synthetic route:

Salt metathesis from anhydrous halides and s-block transfer agents



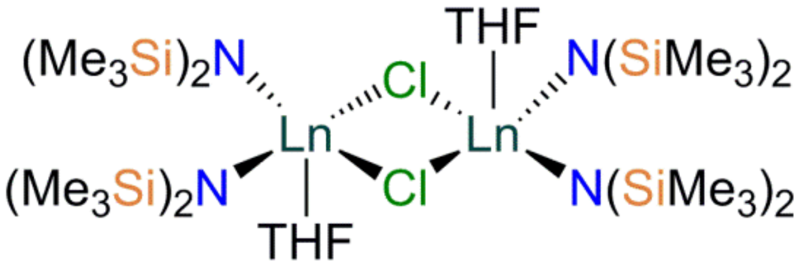
Numerous other routes include ligand substitution, protonolysis, oxidation, reduction, etc.

N-Donor Ligands: Alkylamides



$[Ln(N(SiMe_3)_2)_3]$

Homoleptic

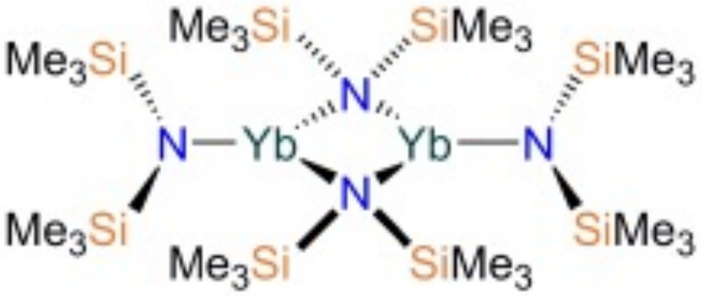


$[Ln(N(SiMe_3)_2)_2(Cl)(THF)]_2$

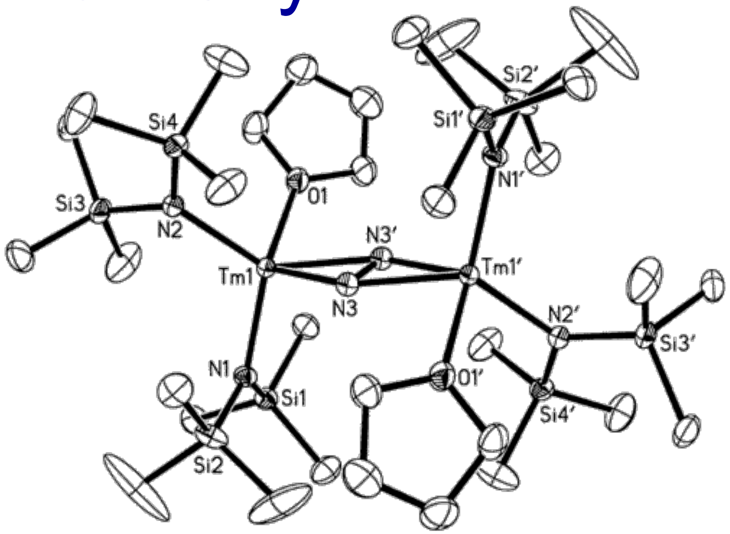
Heteroleptic

$[Ln\{N(SiMe_3)_2\}_3]$ pyramidal in the solid state (agostic interaction Si-C---Ln))
but planar in solution

Accessible also in the +2 oxidation state
Can act as good precursors of other
Organometallic compounds



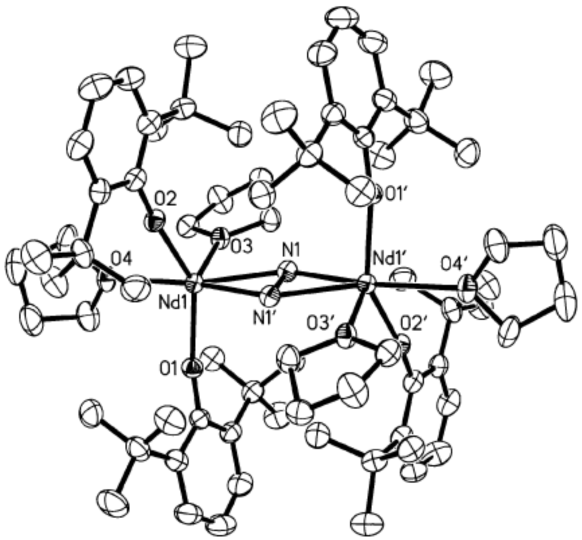
Alkylamides and Aryloxides as convenient supporting ligands in Ln(II) chemistry



$TmI_2(THF)3 + 2 Na(N(SiMe3)_2)$

$\xrightarrow[\text{THF/N}]{}$

$[\{Tm(THF)(N(SiMe_3)_2)_2\}_2(N_2)]$



$NdI_2 + 2 KOC_6H_3{}^tBu_2\text{-}2,6$ (KOAr)

$\xrightarrow[\text{THF/N}_2]{}$

$[\{Nd(THF)_2(OAr)_2\}_2(N_2)]$

O-Donor ligands: alkoxide, phenoxide and siloxides

Synthesised by salt metathesis from anhydrous halides and KOAr salts or protonolysis of Ln-amides and Ln-alkoxides protonolysis primarily but may also be prepared from elemental Ln:

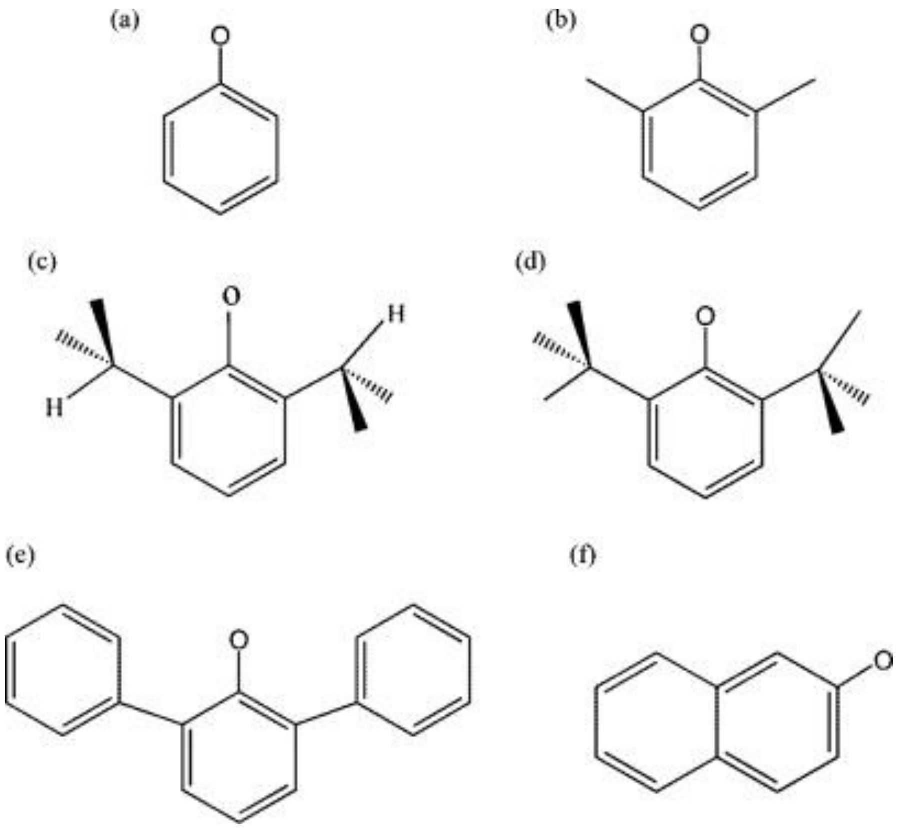
$Ln(N(SiMe_2))_3 + 3\ HOR \rightarrow [Ln(OR)_3] + 3\ HN(SiMe_2)$ **protonolysis**

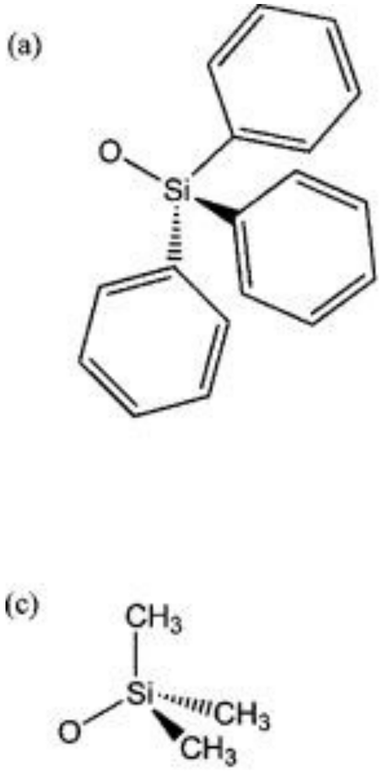
$LnX_3 + 3\ KOR \rightarrow [Ln(OR)_3] + 3KX$ **salt metathesis**

$Y + 3\ ROH \rightarrow [Y(ORi)_3] + 1.5\ H_2$ **oxidation**

R. Anwander, *Topics Curr. Chem.*, **1996**, *179*, 149

O-Donor Ligands: Aryloxides and Siloxides





Siloxides less basic donor:
More innocent ligands

Boyle Chem. Rev. 2008, 108, 1896–1917

O-Donor ligands: alkoxide, phenoxide and siloxides

O-donor tend to form polynuclear compounds via bridging O

The size of alkoxide clusters depends upon the size of the R-groups:

$[Nd(OCH_2But)_3]_4$ $[La(OBut)_3]_3$ $[Ce(OCPh_3)_3]_2$

Bulky Ligands aryloxides can be used to isolate monomeric complexes

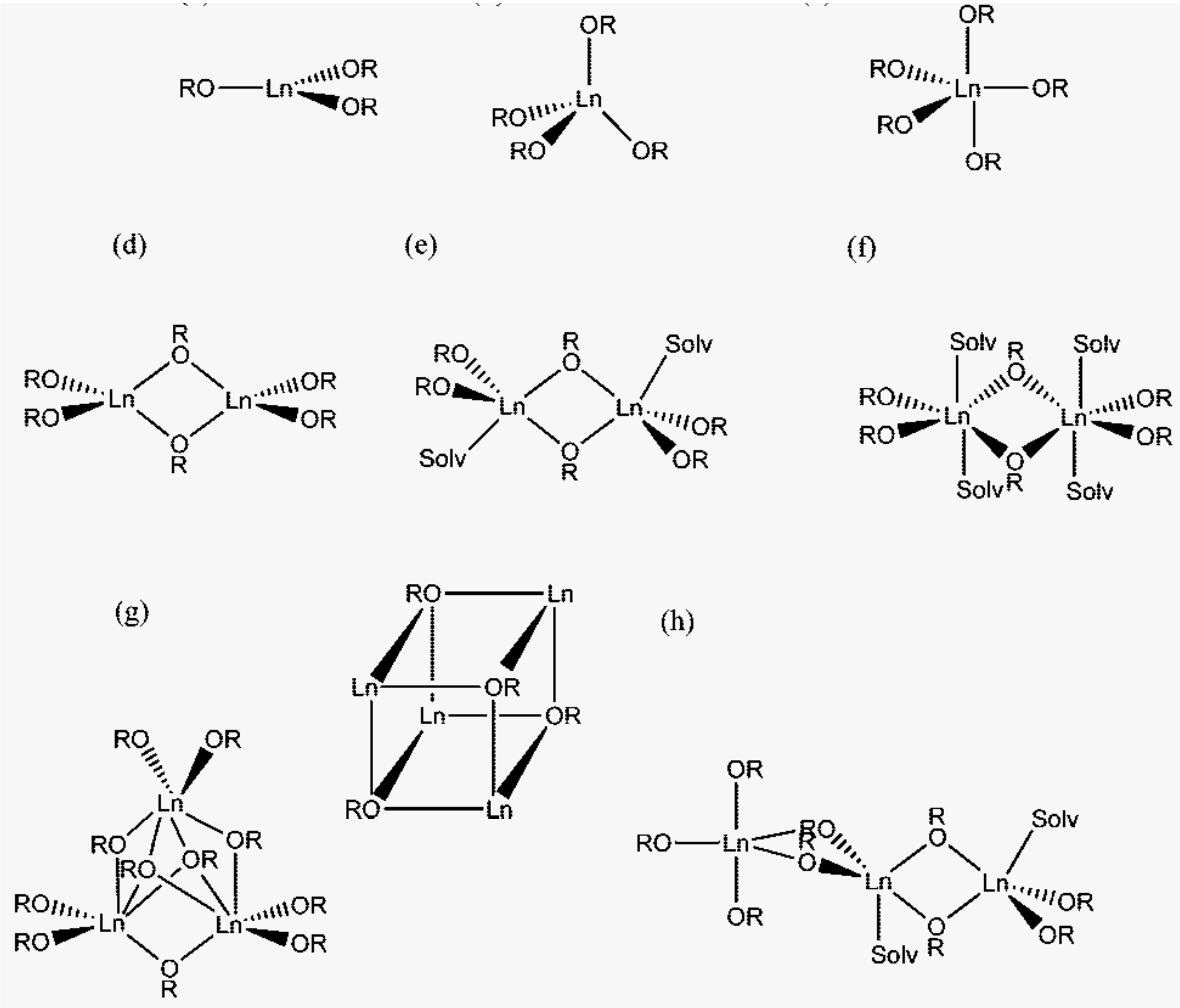
$[Yb(OC_6H_2But_3\text{-}2,4,6)_3]$

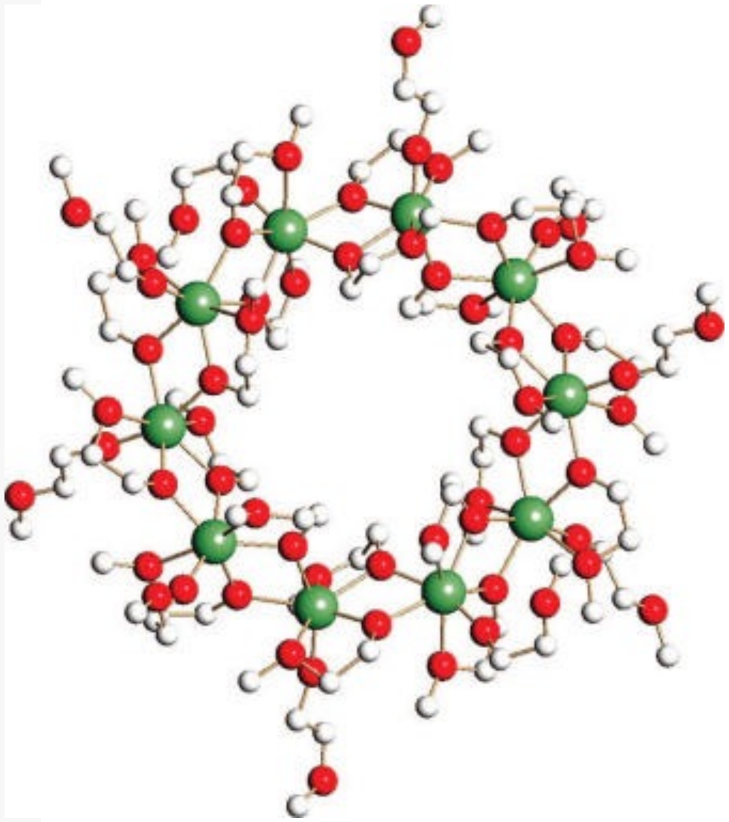
Can also be used to prepare complexes of divalent lanthanides

$[Yb_2^{II}(OC_6H_3Ph_2\text{-}2,6)(\mu\text{-}OC_6H_3Ph_2\text{-}2,6)_3]$

R. Anwander, *Topics Curr. Chem.*, **1996**, *179*, 149

Aryloxides Complexes: Polymetallic complexes





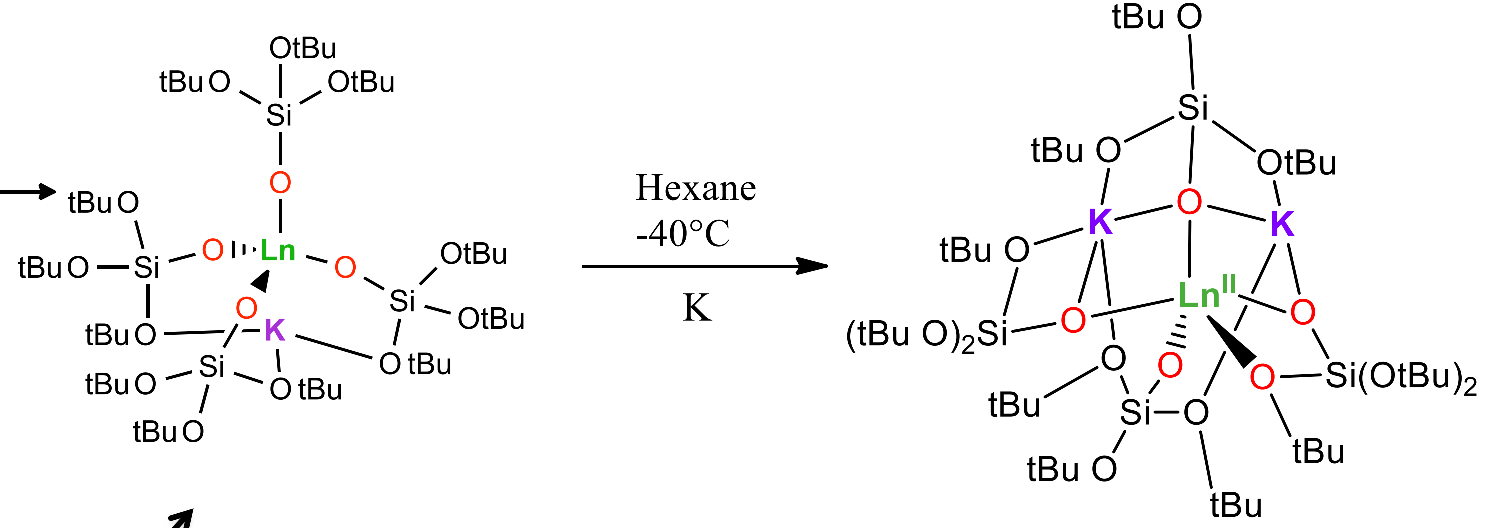
$[Dy(\mu\text{-}OEtOMe)_2(OEtOMe)]_{10}$.

Depending of the size of R different nuclearity clusters can be obtained
In coordinating solvents smaller compounds are formed

“ate” complexes of Aryloxides and Siloxides

$LnX_3 + 4\ KL \xrightarrow[-3KX]{THF}$

Ln=Sm, Eu, Yb

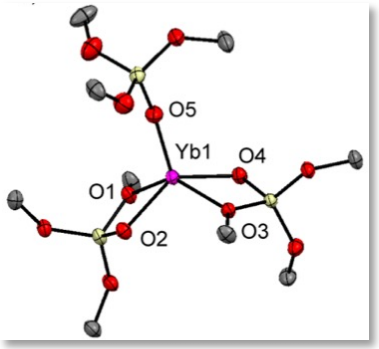


Salt metathesis

$LnX_3 + 3\ KOSi(OtBu)_3 \not\longrightarrow Ln(OSi(OtBu)_3)_3$

Stable Ln(II) Complexes are also formed

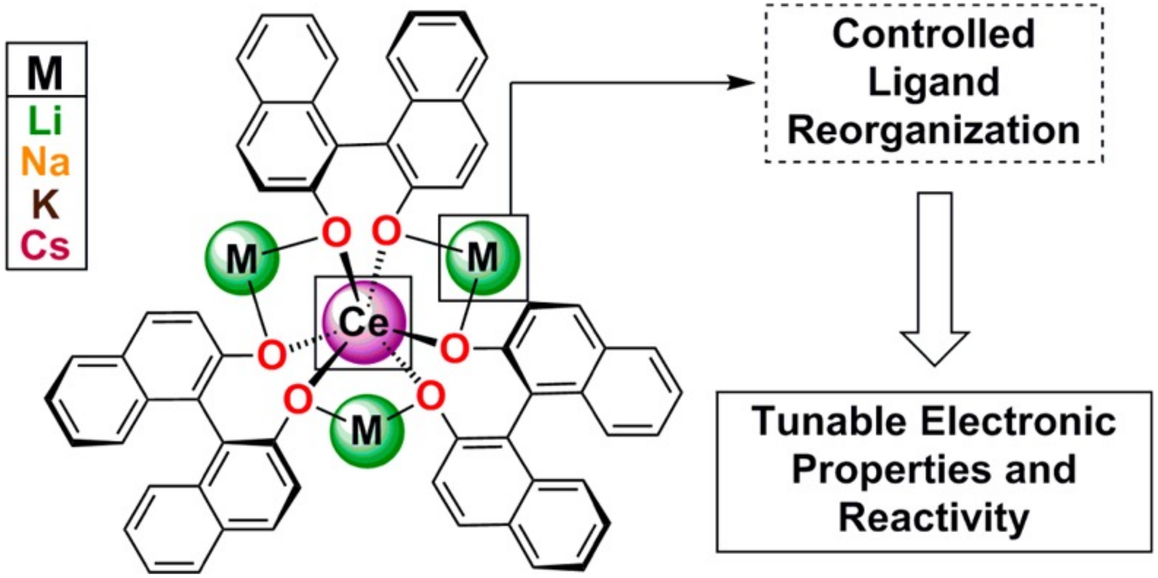
$Ln(N(SiMe_2))_3 + 3\ HOSi(OtBu)_3 \longrightarrow$



protonolysis

“ate” complexes of Aryloxides and Siloxides

$CeX_3 + 3\,(RO_2^{2-})M_2 \longrightarrow$



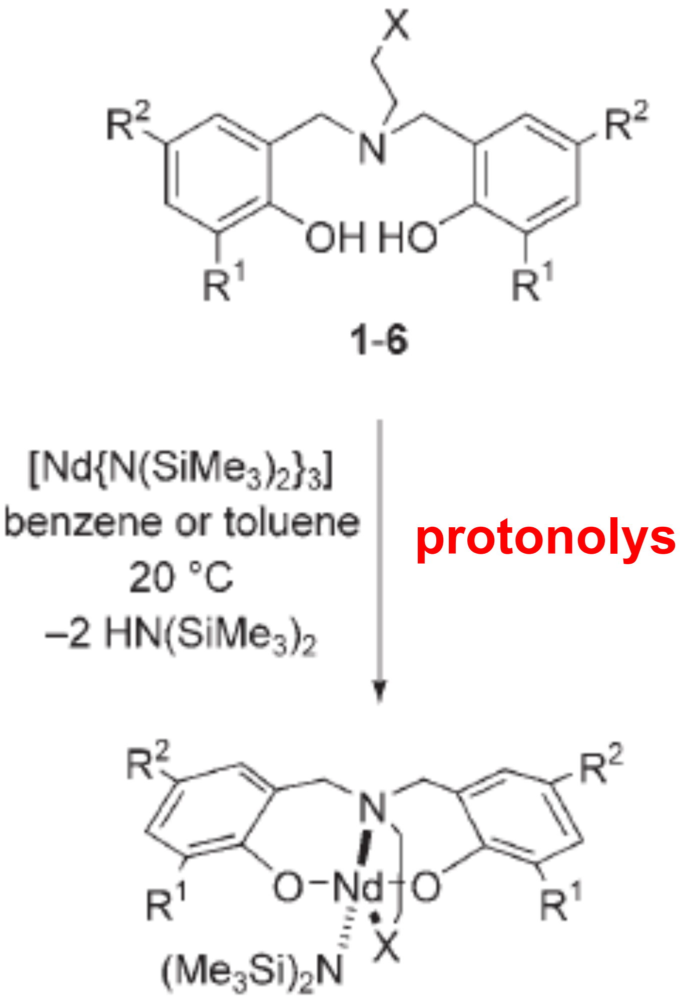
The electronic properties of the Ce^{III} and Ce^{IV} compounds are tuned by the Lewis acidity of M.

The nature of the cation also affects the reorganisation of the ligands during inner-sphere reactivity
Ligands reorganisation is key during Ce^{III} oxidation reactions

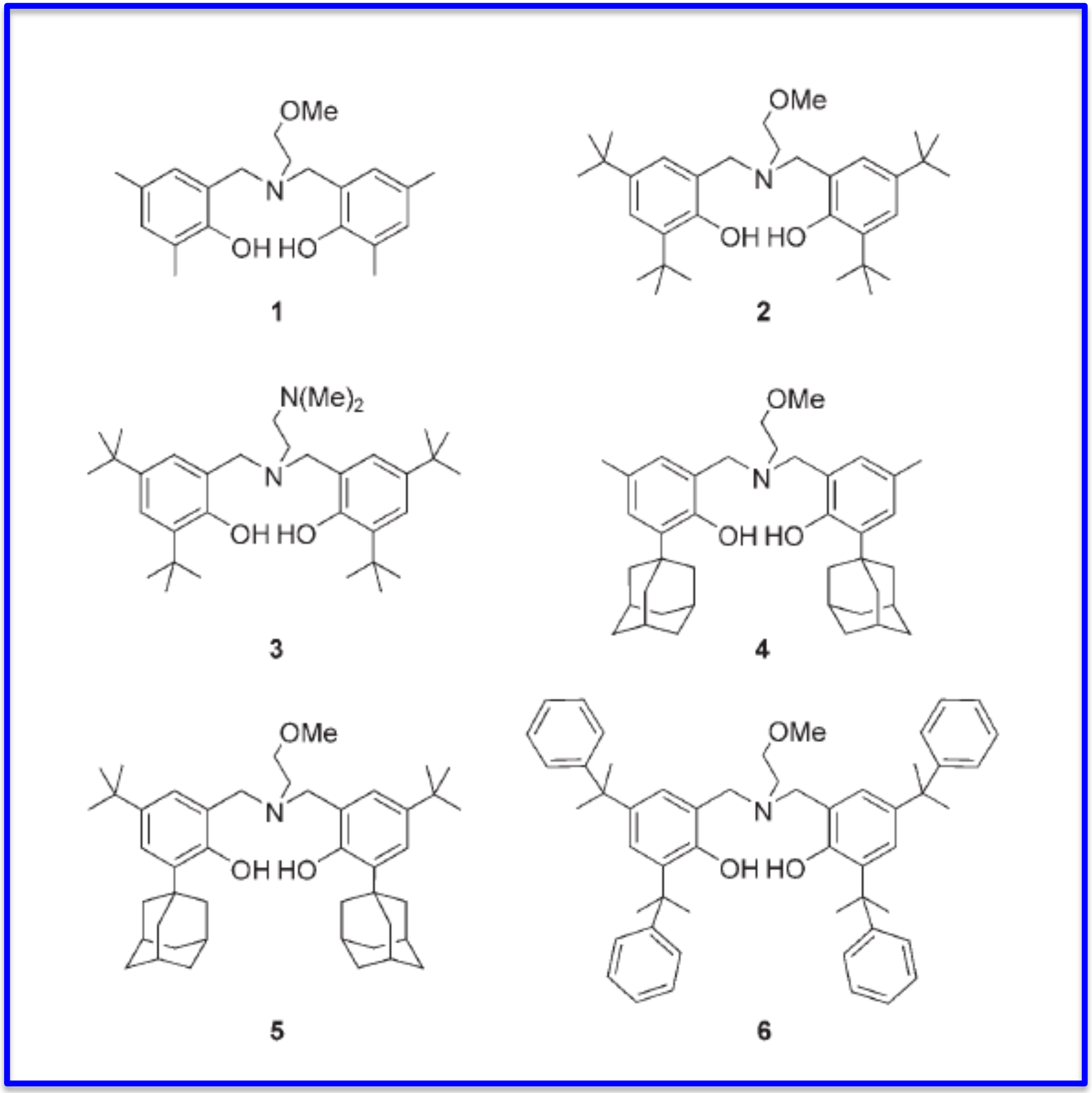
The coordinated alkali metal plays an important role in structure and reactivity

Schelter E. JACS 14

O,N-Donor Ligands: Bis-Phenolates



protonolysis



Chem. Eur. J. 2006, 12, 169 – 179

Multiple Bonding

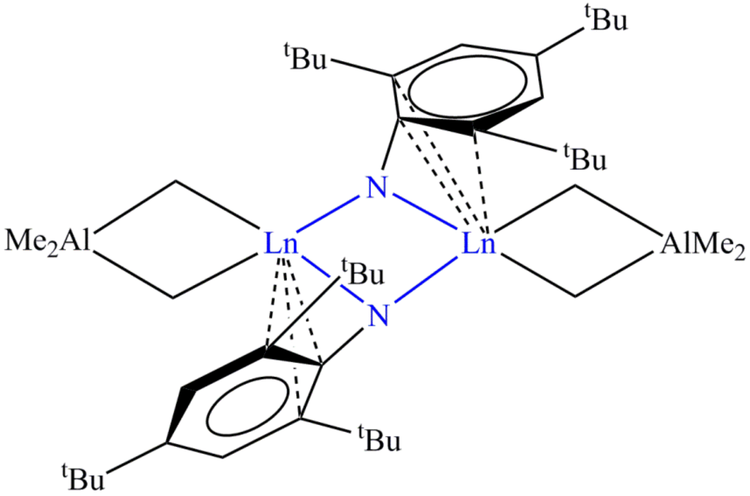
Terminal Ln=E (E = C, N, P, O, S etc.)
multiple bonds rare compared to TM=E analogues.

Attributed to high Ln 5d$_{\pi}$ orbital energies vs low np$_z$ energies.

More reactive because more polarized

Lanthanide imido complexes are postulated as important targets (potential catalytic applications eg nitrogen-based heterocycles).

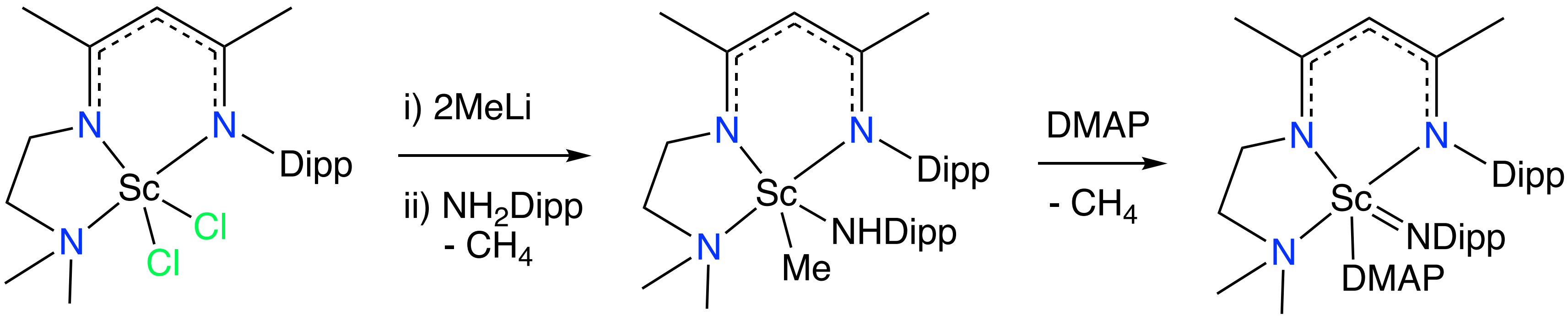
Ln=NR: Most to date are bridging



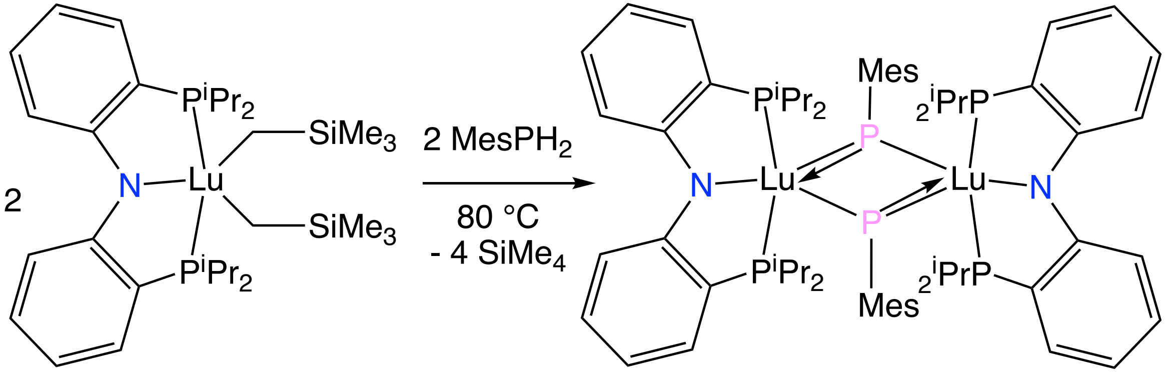
Ln = Y (**14**), La (**15**), Nd (**16**), Lu (**17**)

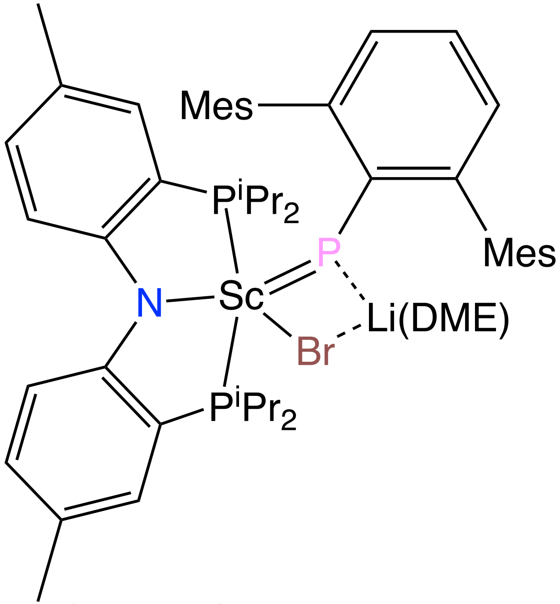
RSC Adv., 2013, 3, 6682–6692

Multiple Bonding



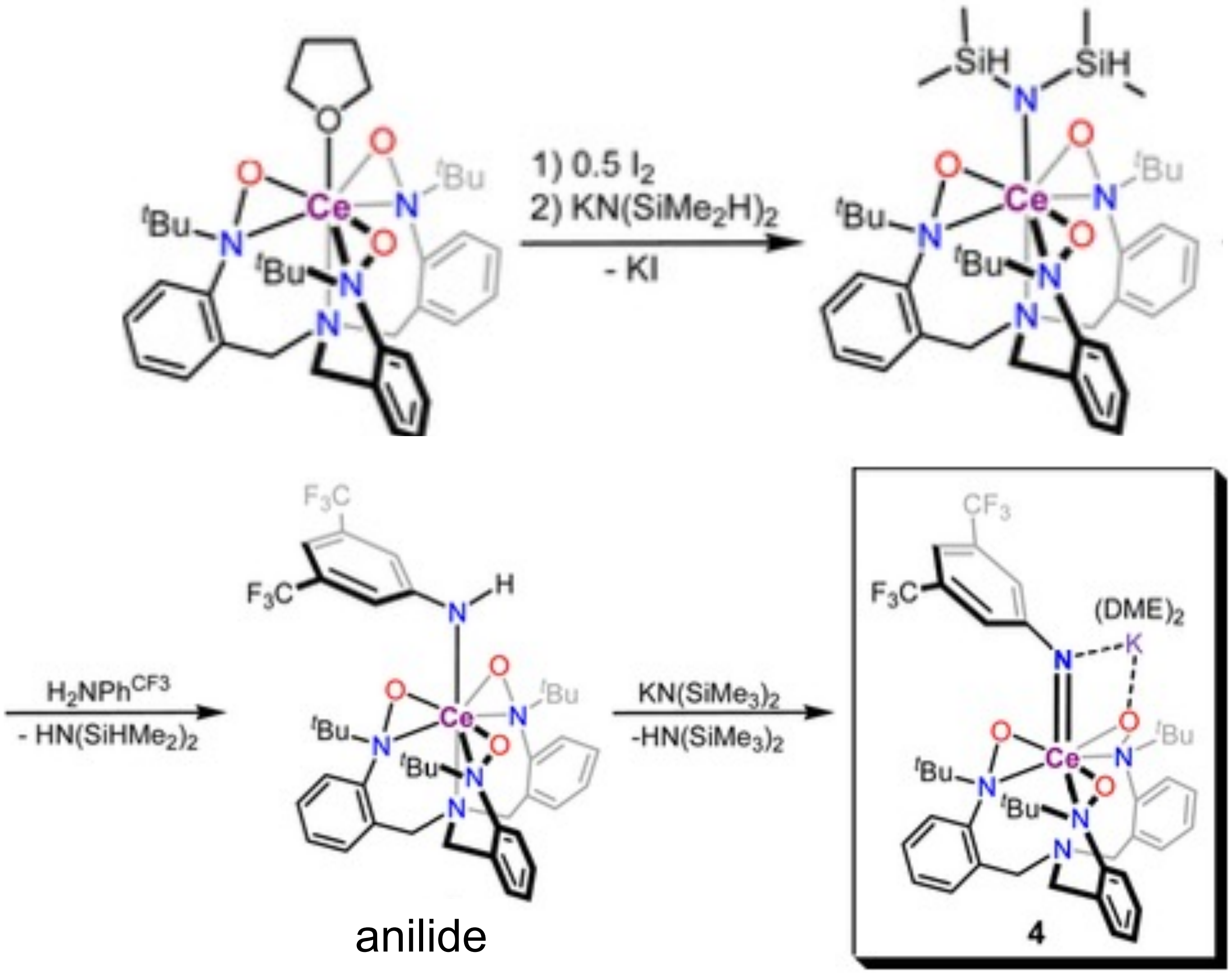
Ln=PR bonds, phosphinidenes





O. T. Summerscales, J. C. Gordon, RSC Adv., 2013, 3, 6682; Y. Chen, Chem. Commun., 2010, 4469.

Multiple Bonding: Cerium imide



amide

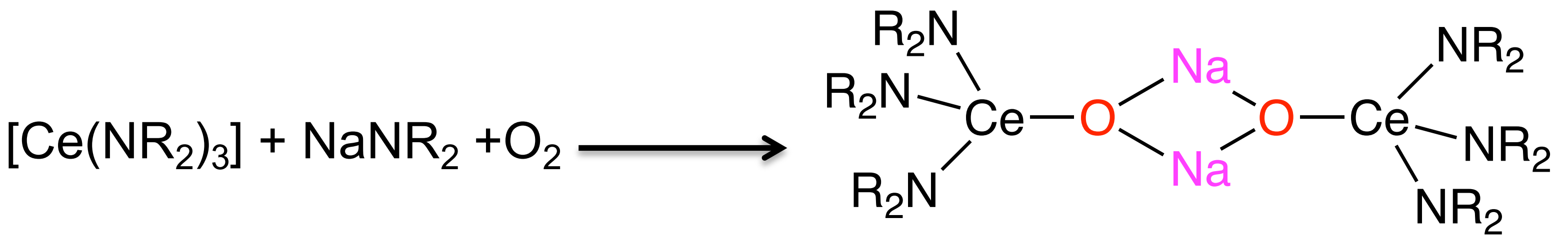
anilide

Supporting ligand
tris(hydroxylaminato)

Schelter
J. Am. Chem. Soc. 2016, 138, 6928−6931

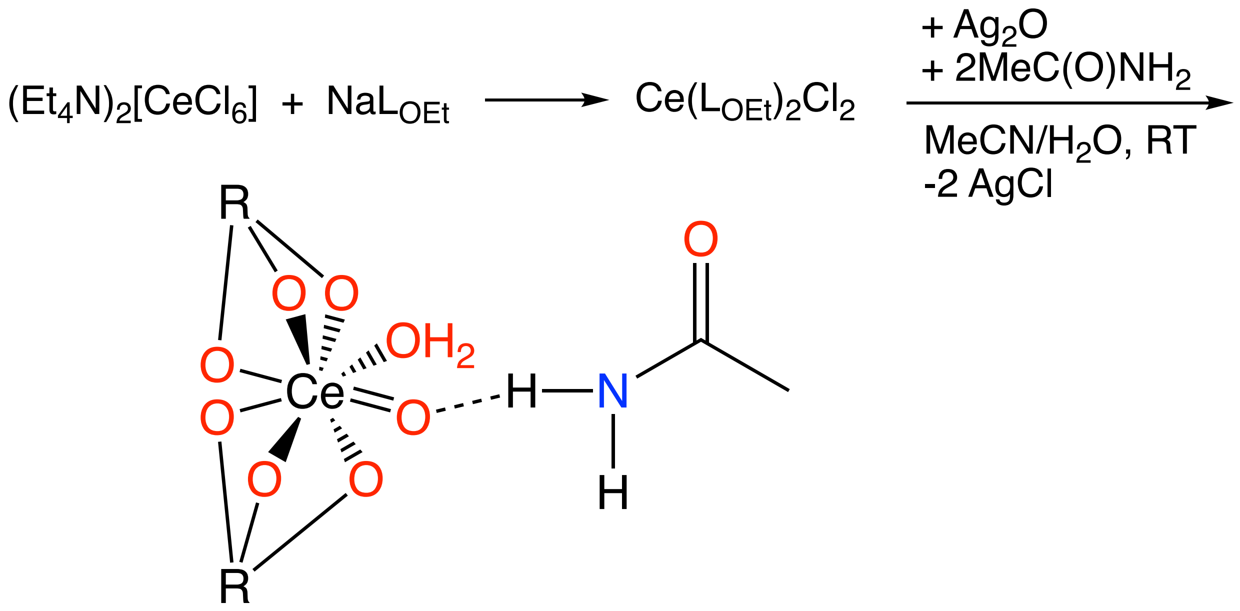
Multiple Bonding

One terminal Ce=O reported : Highly polarized bond Ce^{+}-O^{-} ,
Highly nucleophile oxo group
All other Ln Oxo-complexes are bridging

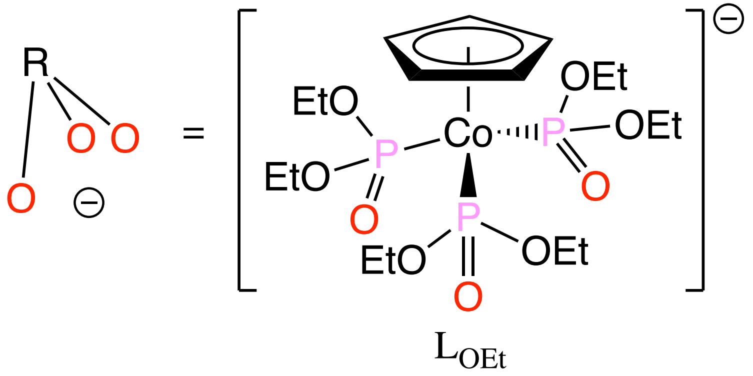


Ce=O = 1.948Å

Dalton Trans., 2010, **39**, 6780–6788

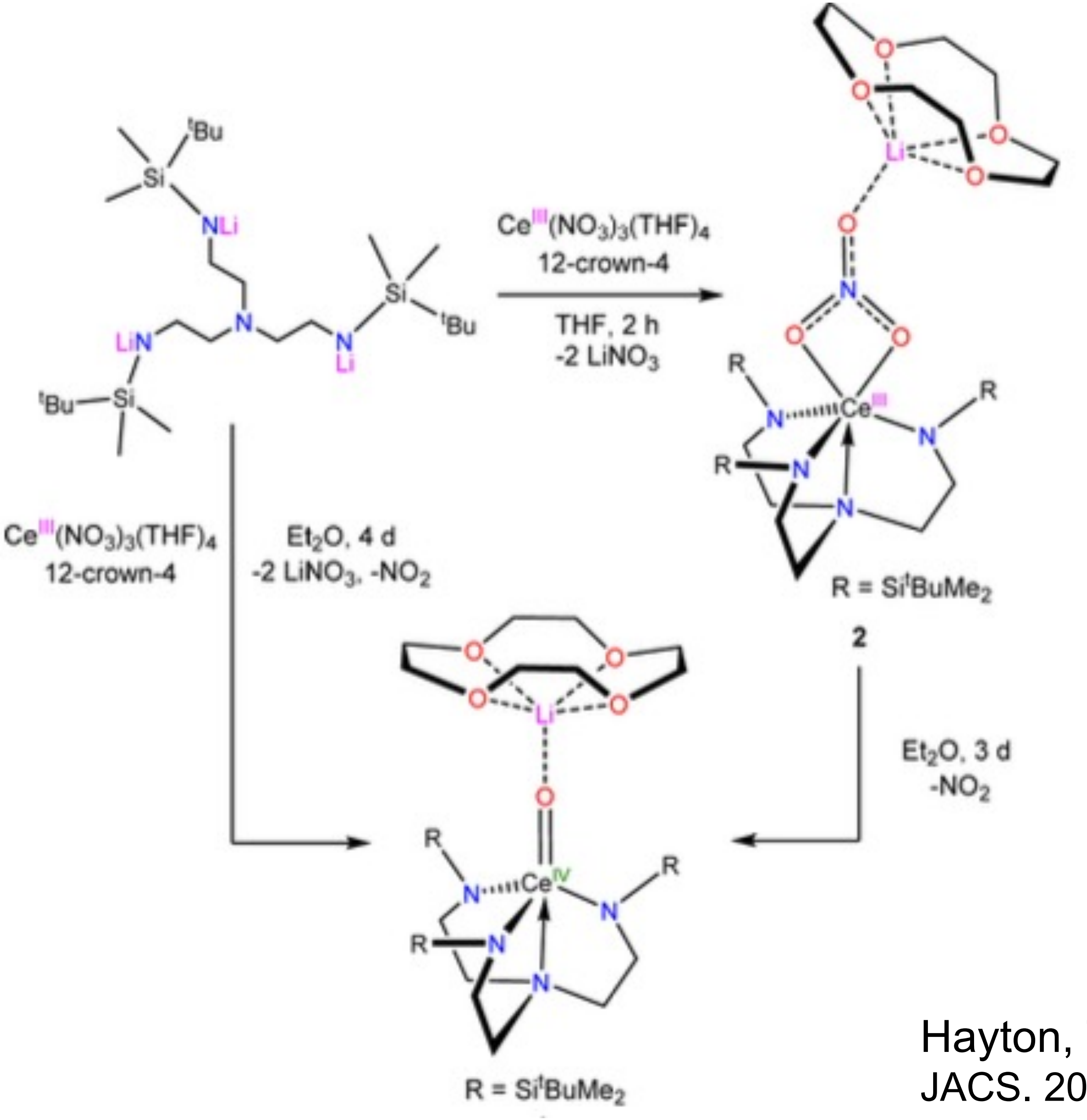


Kläui ligand



Ce=O = 1.857(3) Å   W.-H. Leung, *Angew. Chem. Int. Ed.*, **2014**, *53*, 1626

Formation of a Ce(IV) Oxo Complex via Inner Sphere Nitrate Reduction



Hayton, T
JACS. 2016, 138, 12743−12746

Learning Outcomes

-Negative O donors and rare cases of negative N donors form stable complexes in water
Heterocyclic polydentate N-donors can form complexes in water
Amide and other N donors, phenoxide, alkoxide, siloxide form stable complexes in organic solvents

-Later Ln(III) have higher charge density: higher complex stability

-Polydentate ligands form more stable complexes due to chelate effect

-Most common coordination numbers 8-9 and geometries P, SA, TTP, but common 6-12

-Very bulky ligands (secondary sphere) promote low NC.

-Ln form oxo and hydroxo complexes in presence of water and basic ligands due to their high lewis acidity, hydroxides activate CO_2 to afford carbonates

-Most common synthetic strategies: salt metathesis, protonolysis, oxidation

-Ln do not form terminal multiple bonds due to the high energy of d orbitals
synthetic routes to rare examples exist of Ln=X bonds