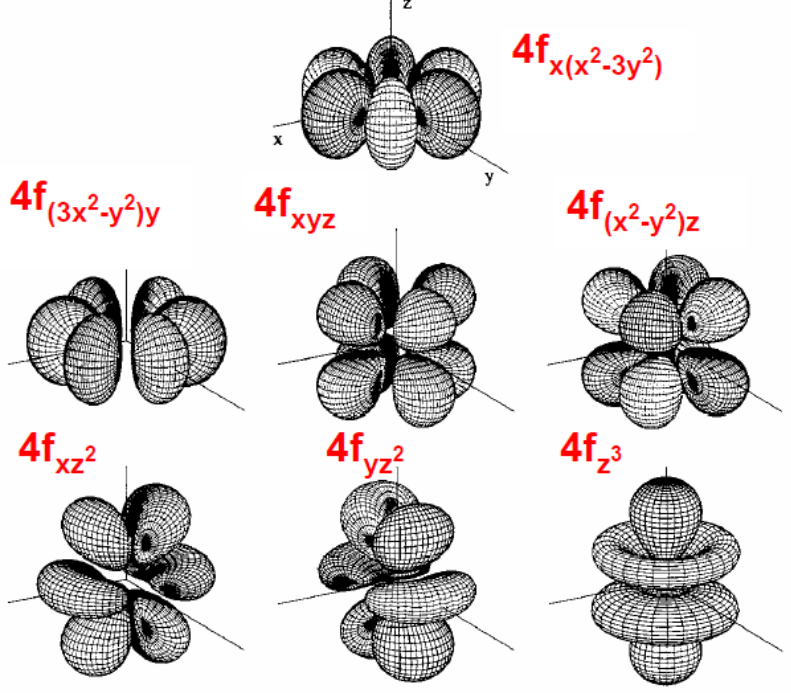
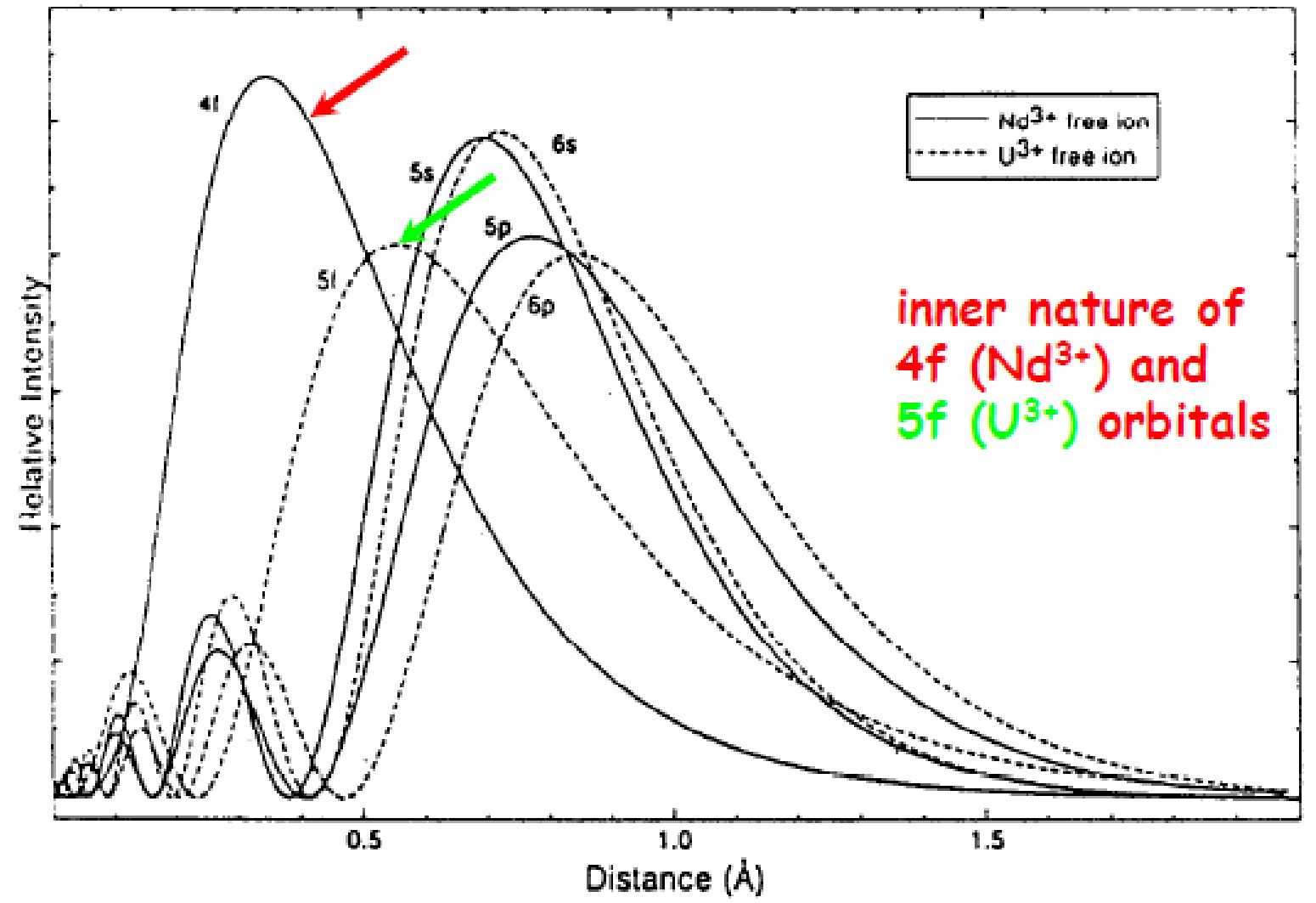


Семинар 8

Соединения лантанидов в степени окисления +2

Что является причиной?



C.Housecroft, A.G.Sharpe Inorganic Chemistry 4-е издание 2012 год

Element name	Symbol	Z	Ground state electronic configuration		
			Ln	Ln^{2+}	Ln^{3+}
Lanthanum	La	57	$[Xe]6s^2 5d^1$	$[Xe]5d^1$	$[Xe]4f^0$
Cerium	Ce	58	$[Xe]4f^1 6s^2 5d^1$	$[Xe]4f^2$	$[Xe]4f^1$
Praseodymium	Pr	59	$[Xe]4f^3 6s^2$	$[Xe]4f^3$	$[Xe]4f^2$
Neodymium	Nd	60	$[Xe]4f^4 6s^2$	$[Xe]4f^4$	$[Xe]4f^3$
Promethium	Pm	61	$[Xe]4f^5 6s^2$	$[Xe]4f^5$	$[Xe]4f^4$
Samarium	Sm	62	$[Xe]4f^6 6s^2$	$[Xe]4f^6$	$[Xe]4f^5$
Europium	Eu	63	$[Xe]4f^7 6s^2$	$[Xe]4f^7$	$[Xe]4f^6$
Gadolinium	Gd	64	$[Xe]4f^7 6s^2 5d^1$	$[Xe]4f^7 5d^1$	$[Xe]4f^7$
Terbium	Tb	65	$[Xe]4f^9 6s^2$	$[Xe]4f^9$	$[Xe]4f^8$
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$	$[Xe]4f^{10}$	$[Xe]4f^9$
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$	$[Xe]4f^{11}$	$[Xe]4f^{10}$
Erbium	Er	68	$[Xe]4f^{12} 6s^2$	$[Xe]4f^{12}$	$[Xe]4f^{11}$
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$	$[Xe]4f^{13}$	$[Xe]4f^{12}$
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$	$[Xe]4f^{14}$	$[Xe]4f^{13}$
Lutetium	Lu	71	$[Xe]4f^{14} 6s^2 5d^1$	$[Xe]4f^{14} 5d^1$	$[Xe]4f^{14}$

С чего все началось?

Eu(II), Yb(II), Sm(II) 1906

Chem. Rev. **1988**, *88*, 93– 107,
DOI: 10.1021/cr00083a005

Ln	Eu	Yb	Sm	Tm	Dy	Nd
$E°(Ln^{3+}/Ln^{2+})/V$	–0.35	–1.05	–1.55	–2.3	–2.5	–2.6

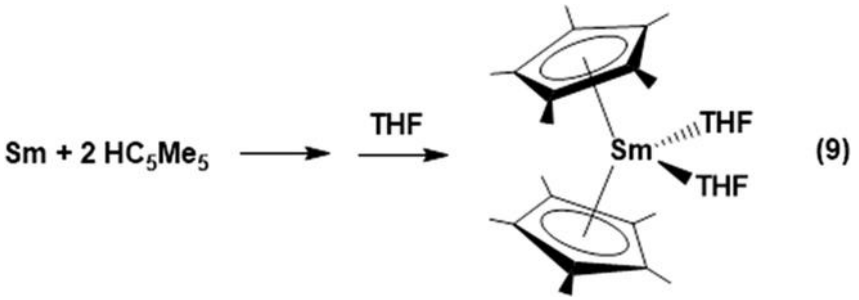
$$Ln + NH_4X \xrightarrow[-H_2]{\text{liq. } NH_3} LnI_2$$

Ln = Eu, Yb, X = Cl, Br, I

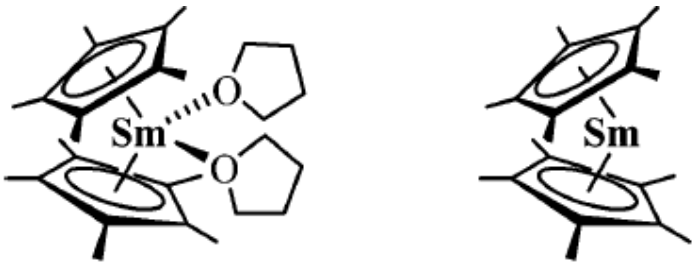
Table 1. Estimated Ln^{3+}/Ln^{2+} Standard Reduction Potentials (±0.2 V) of Yttrium and the Lanthanides Based on Experimental, Spectroscopic, and Thermodynamic Data[10]

Ln	potential (V vs SHE)	Ln	potential (V vs SHE)
Eu	−0.35	Pr	−2.7
Yb	−1.15	Y	−2.8
Sm	−1.55	Ho	−2.9
Tm	−2.3	Er	−3.1
Dy	−2.5	La	−3.1
Nd	−2.6	Ce	−3.2
Pm	−2.6	Tb	−3.7
Lu	−2.7	Gd	−3.9

Самарий 2+ - самый реакционноспособный?



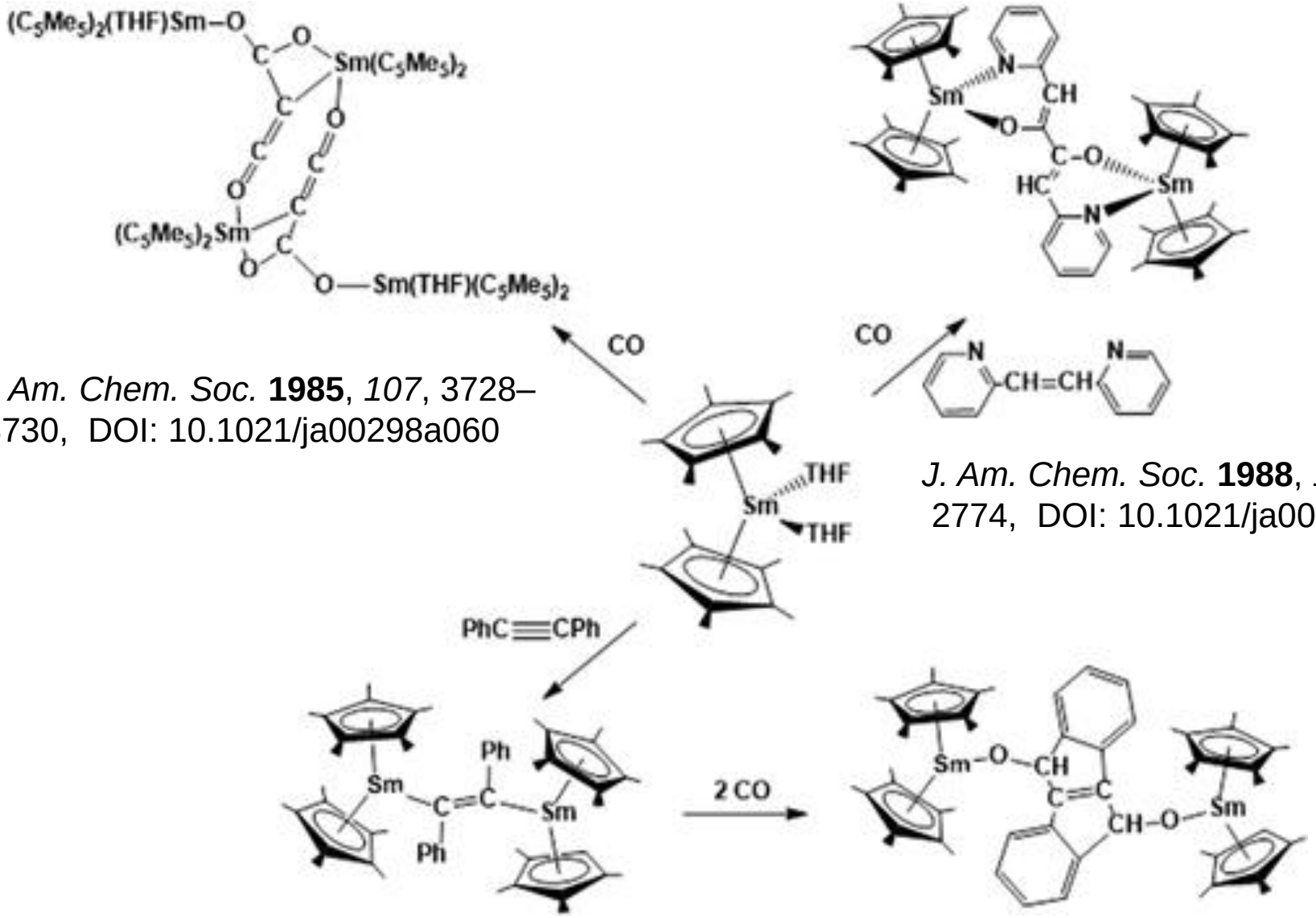
J. Am. Chem. Soc. **1981**, *103*, 6507– 6508, DOI: 10.1021/ja00411a046



$(C_5Me_5)_2Sm(THF)_2$ **$(C_5Me_5)_2Sm$**

$SmI_2 + 2KC_5Me_5 = (C_5Me_5)_2Sm(THF)_2$

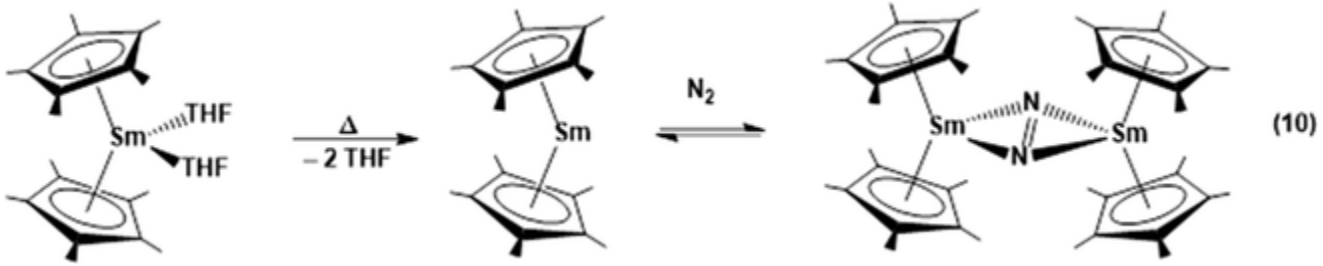
J. Am. Chem. Soc. **1985**, *107*, 941– 946, DOI: 10.1021/ja00290a032



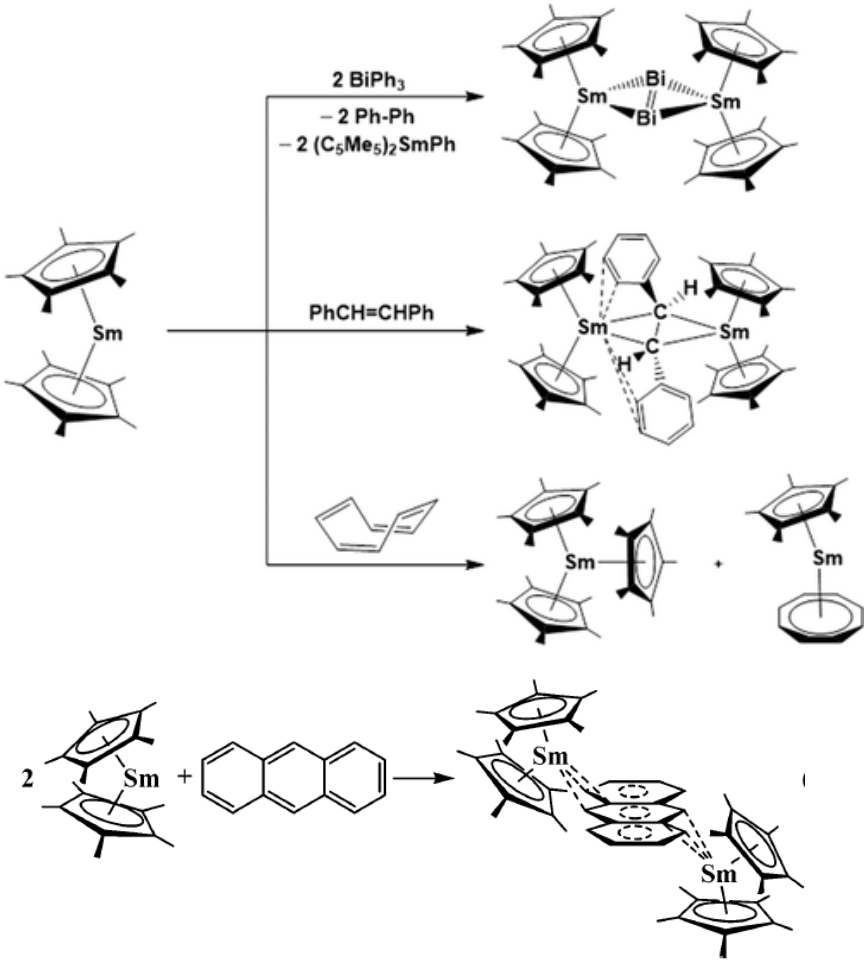
J. Am. Chem. Soc. **1985**, *107*, 3728–3730, DOI: 10.1021/ja00298a060

J. Am. Chem. Soc. **1988**, *110*, 2772–2774, DOI: 10.1021/ja00217a013

J. Am. Chem. Soc. **1986**, *108*, 1722– 1723, DOI: 10.1021/ja00267a071



J. Am. Chem. Soc. **1988**, *110*, 6877– 6879, DOI: 10.1021/ja00228a043



J. Am. Chem. Soc. **1991**, *113*, 9880–9882, DOI: 10.1021/ja00026a040

J. Am. Chem. Soc. **1990**, *112*, 219–223, DOI: 10.1021/ja00157a035

Organometallics **1993**, *12*, 4664–4667, DOI: 10.1021/om00035a062

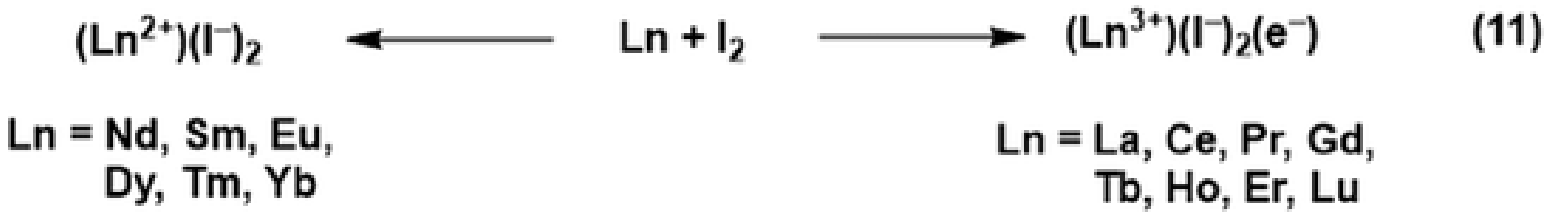
Продолжение ряда Ln^{2+}

$LnHal_2$ Nd (II) 1959, Tm(II) 1960, Dy(II) 1966

$NdCl_2$ *J. Am. Chem. Soc.* **1959**, *81*, 5512– 5512, DOI: 10.1021/ja01529a067

TmI_2 *J. Inorg. Nucl. Chem.* **1960**, *13*, 32– 35, DOI: 10.1016/0022-1902(60)80232-1

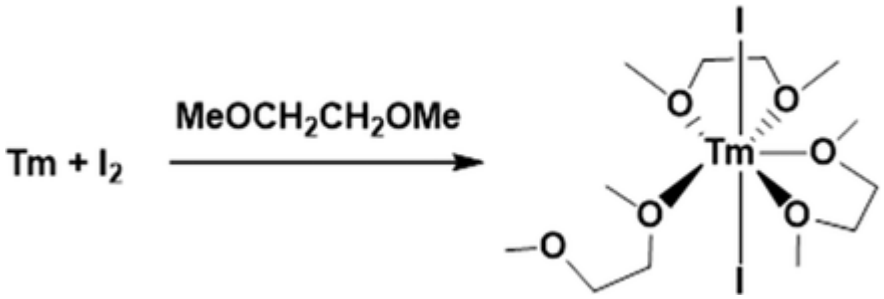
$DyCl_2$ *Inorg. Chem.* **1966**, *5*, 938– 940, DOI: 10.1021/ic50039a050

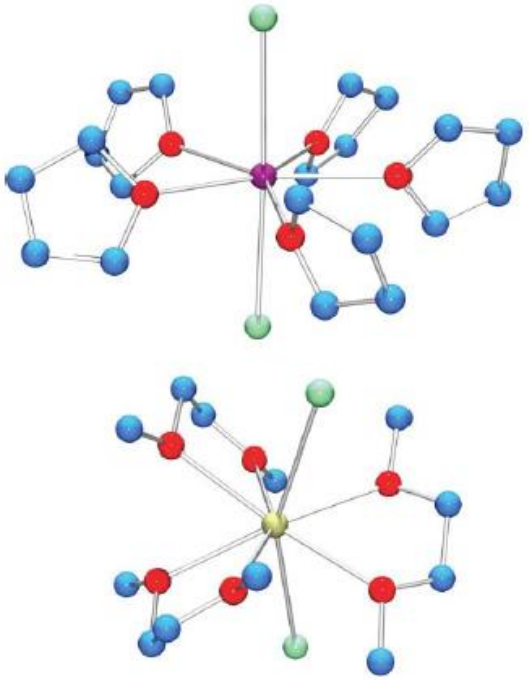


предполагалось, что электрон решетки находится в зоне, образованной 5d-орбиталями

Chem. Mater. **1992**, *4*, 1157– 1168, DOI: 10.1021/cm00024a012

Первые молекулярные комплексы “новых” Ln

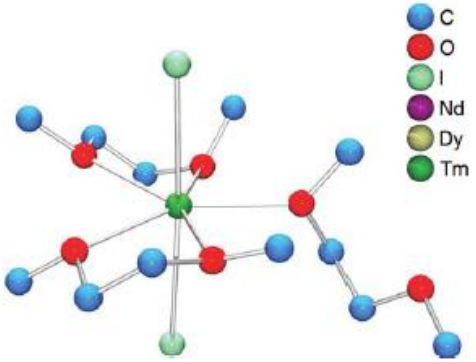




Angew. Chem., Int. Ed. Engl. **1997**, *36*, 133– 135, DOI: 10.1002/anie.199701331

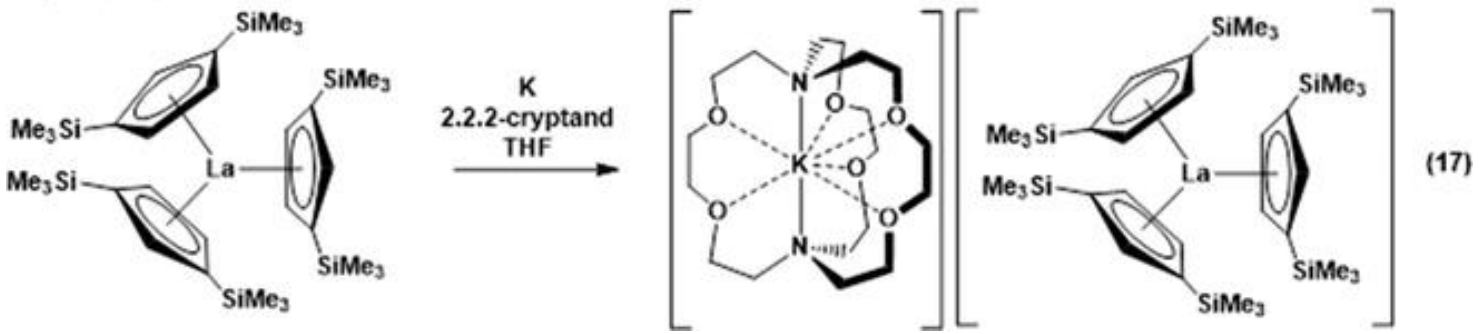
J. Am. Chem. Soc. **2000**, *122*, 11749– 11750, DOI: 10.1021/ja0034949

Dy

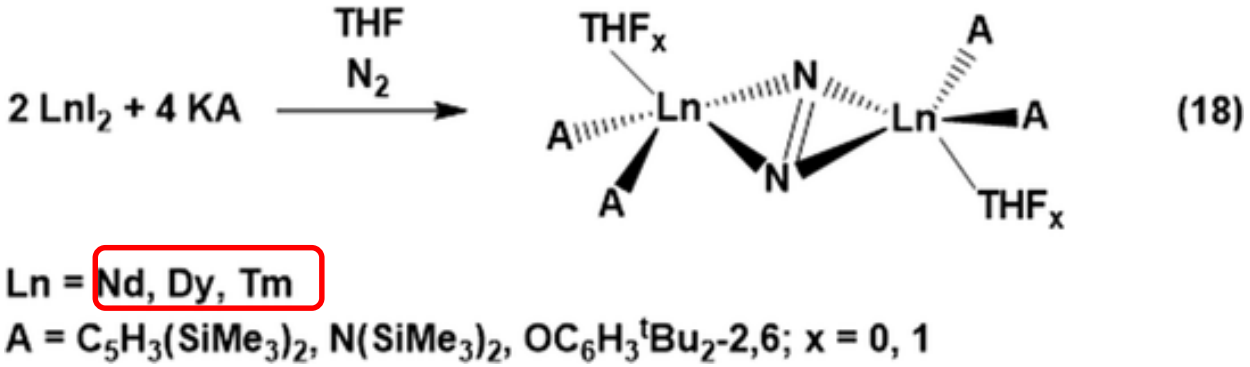


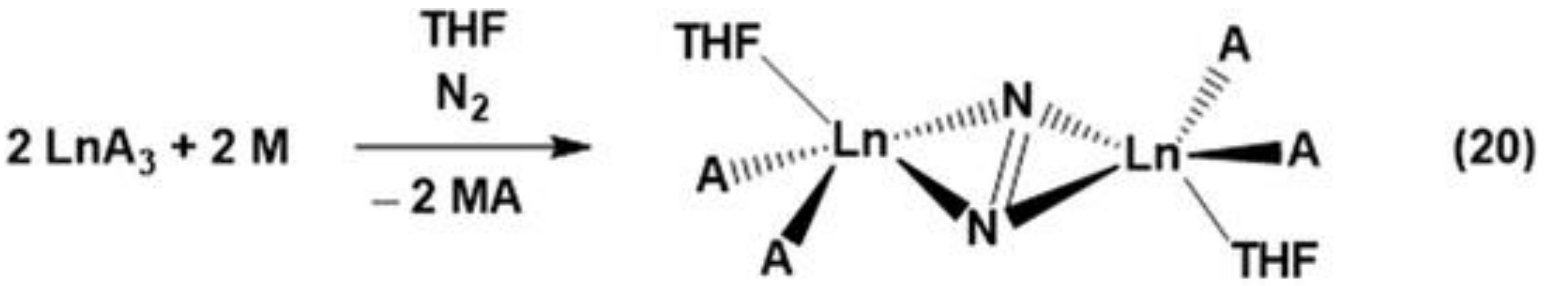
Angew. Chem., Int. Ed. **2001**, *40*, 3176– 3178, DOI: 10.1002/1521-3773(20010903)40:17<3176::AID-ANIE3176>3.0.CO;2-Y

Nd



Angew. Chem., Int. Ed. **2008**, *47*, 1488– 1491, DOI: 10.1002/anie.200704887





Ln = Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu

A = C_5Me_5, C_5Me_4H, $N(SiMe_3)_2$, $OC_6H_3{}^tBu_2$-2,6, $C_5H_3{}^tBu_2$

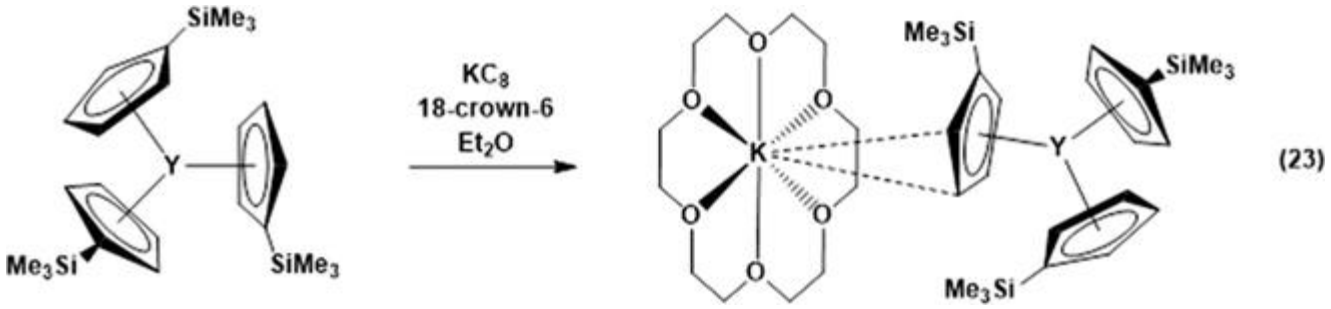
M = K, KC_8…

J. Am. Chem. Soc. **2004**, *126*, 454– 455, DOI: 10.1021/ja036923m

Angew. Chem., Int. Ed. **2004**, *43*, 5517– 5519, DOI: 10.1002/anie.200461170

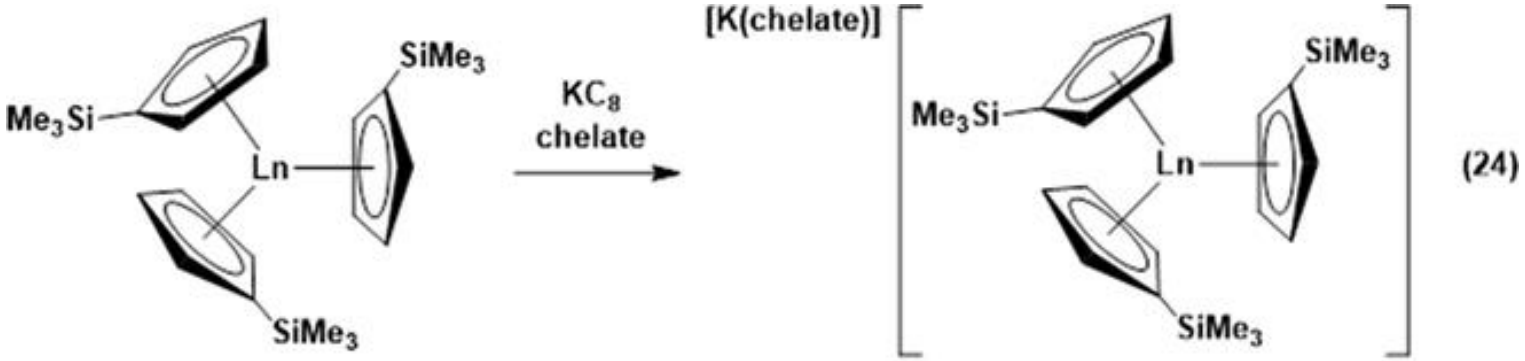
Молекулярные металлоорганические соединения Ln^{2+}

$[(18\text{-Crown-6})K][(C_5H_4SiMe_3)_3Y]$



(23)

J. Am. Chem. Soc. **2011**, *133*, 15914– 15917, DOI: 10.1021/ja207151y

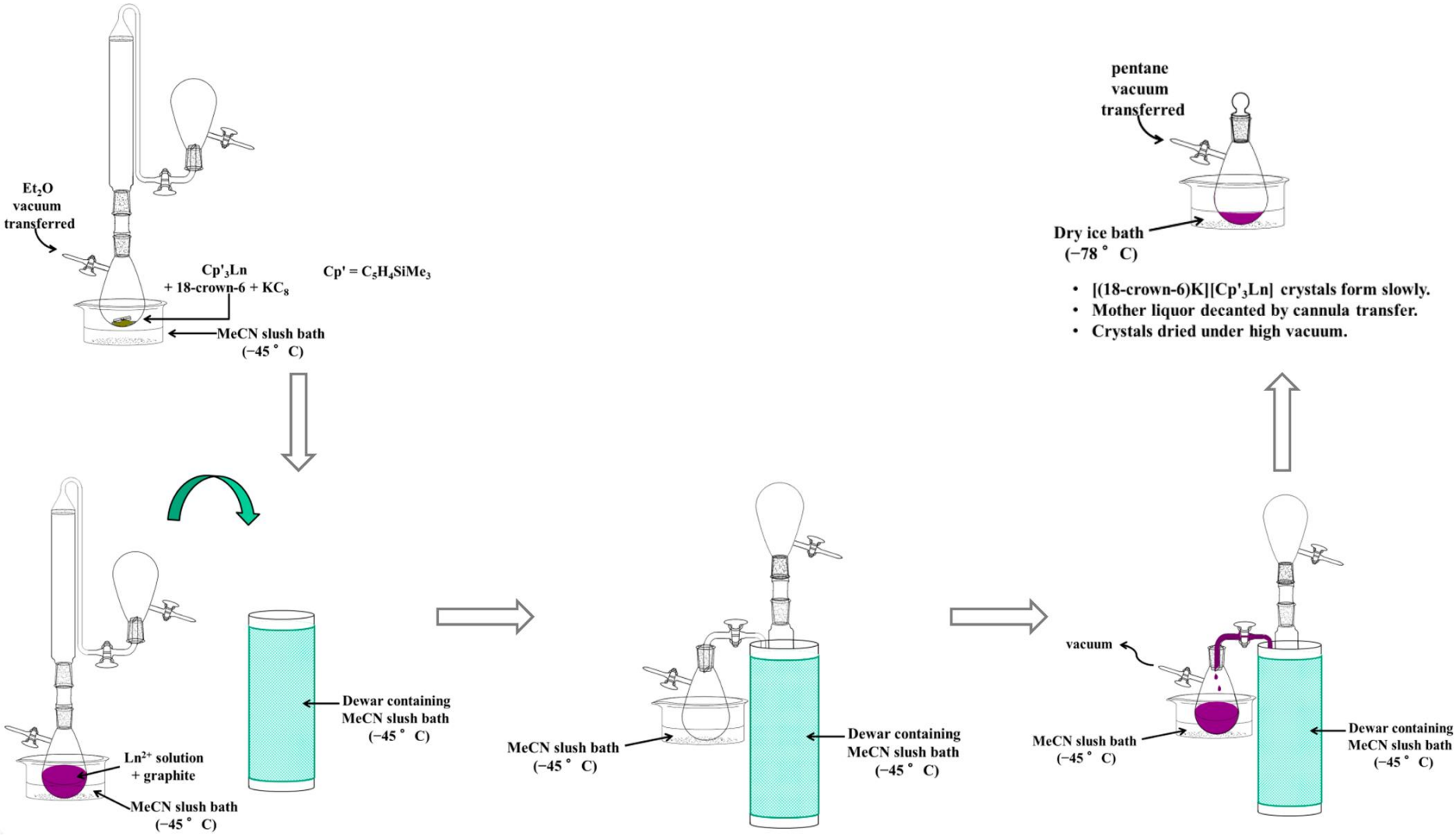


(24)

Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
chelate = 18-crown-6, 2.2.2-cryptand

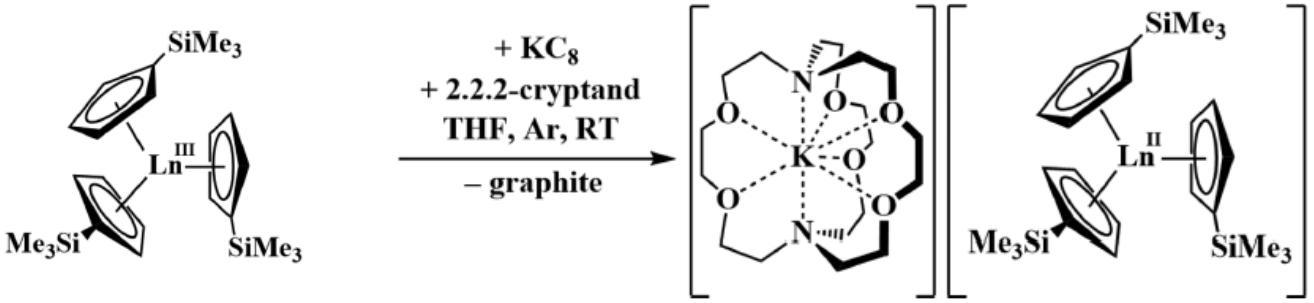
J. Am. Chem. Soc. **2012**, *134*, 8420– 8423, DOI: 10.1021/ja303357w

J. Am. Chem. Soc. **2013**, *135*, 9857– 9868, DOI: 10.1021/ja403753j



Organometallics 2016, 35, 3088−3100 DOI: 10.1021/acs.organomet.6b00466

Органические производные Ln^{2+}

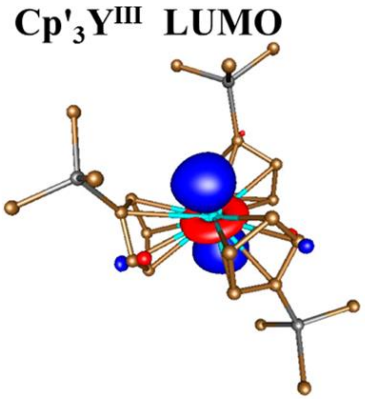


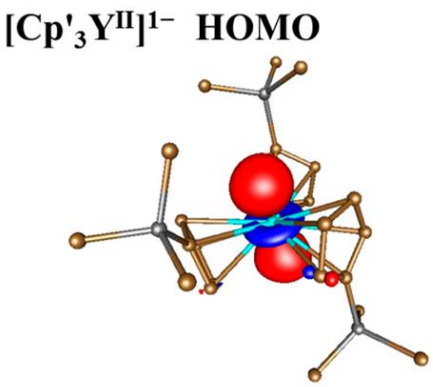
Ln	metal–(ring centroid) distance (Å) Cp'_3Ln (Ln^{3+})	metal–(ring centroid) distance (Å) $(Cp'_3Ln)^-$ (Ln^{2+})	difference in metal–(ring centroid) distance (Å) new Ln^{2+} ions	difference in metal–(ring centroid) distance (Å) traditional Ln^{2+} ions
La	2.559	2.586	0.027	
Ce	2.529	2.558	0.029	
Pr	2.508	2.535	0.027	
Nd	2.489	2.519		0.030
Sm	2.459	2.608		0.149
Eu	2.451	2.607		0.156
Gd	2.437	2.468	0.031	
Tb	2.423	2.454	0.031	
Dy	2.407	2.443		0.036
Y	2.405	2.436	0.031	
Ho	2.394	2.426	0.032	
Er	2.386	2.416	0.030	
Tm	2.379	2.502		0.123
Yb	2.365	2.508		0.143
Lu	2.361	2.392	0.031	

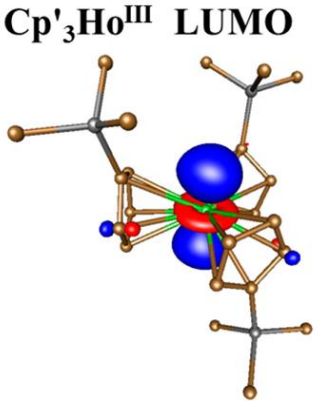
Pr^{2+}, Gd^{2+}, Lu^{2+}

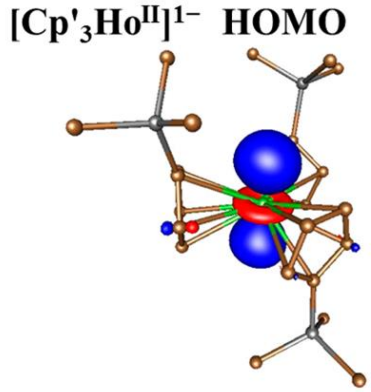
Выбор лиганда и противоиона

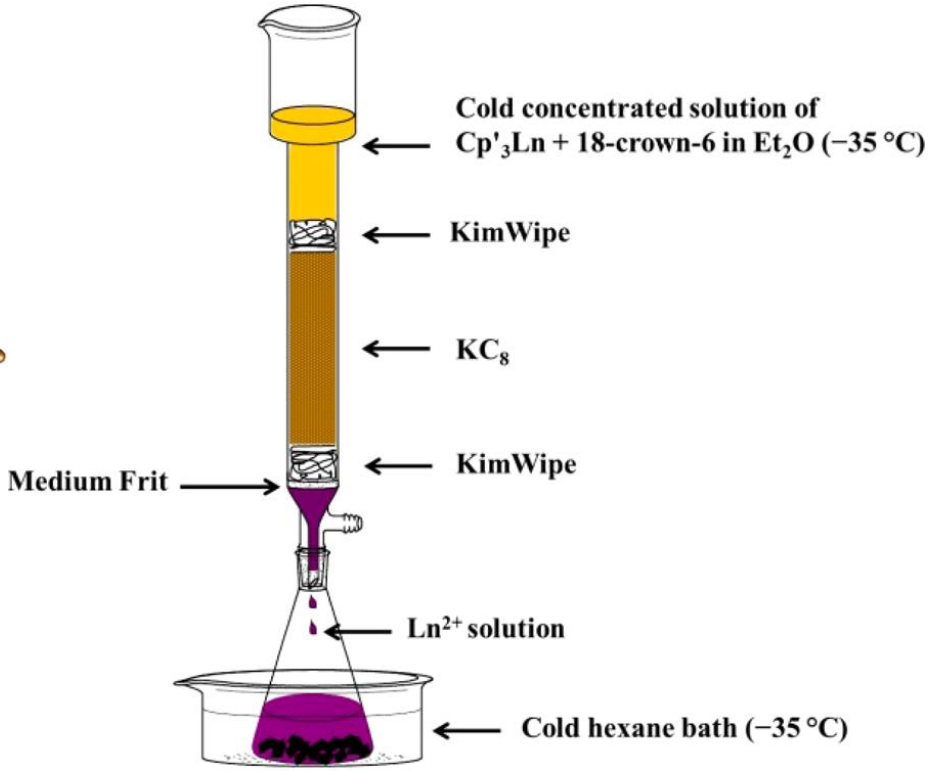
$4f^{n+1}\ 5d^0$ или $4^{fn}\ 5d^1$





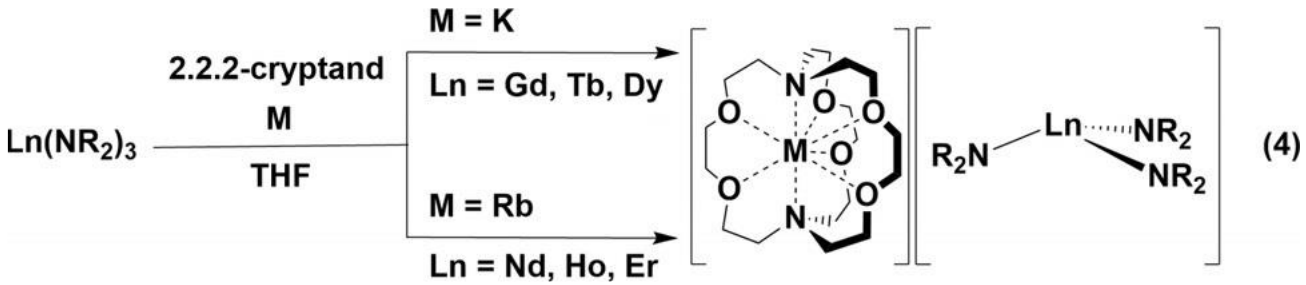






https://youtu.be/CoGFF4YReFo?list=PLEQ2r9YGFNevddQRI17uMMc8Q5HDbuhGh

Не только Ср ?



опровергают два постулата в химии Ln^{2+} : амидные лиганды не образуют Ln^{2+}, Y при восстановлении подобен тяжелым РЗЭ

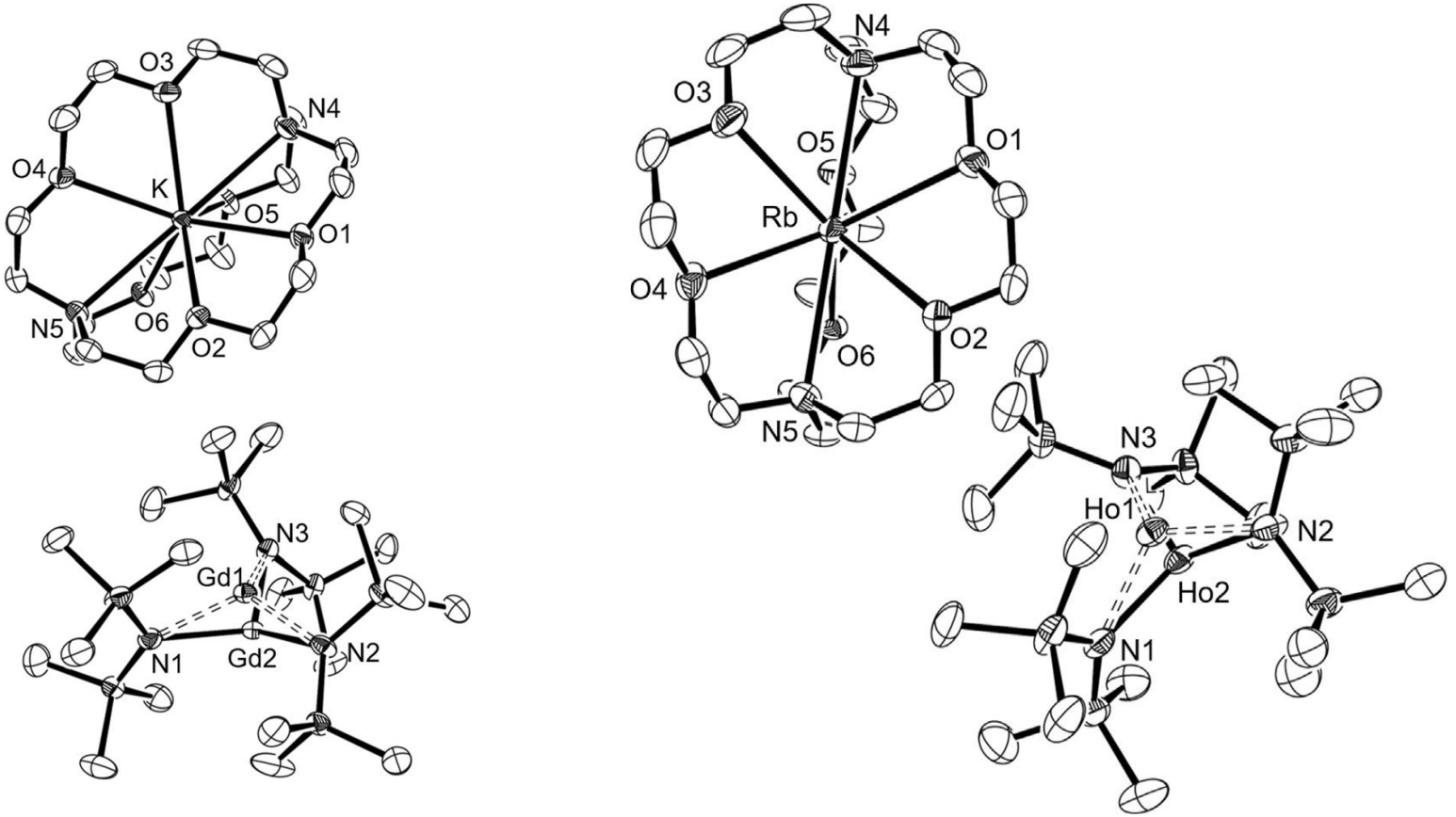
Первоначально предполагалось, что только Eu^{2+}, Yb^{2+}, Sm^{2+}, Tm^{2+}, Dy^{2+}, Nd^{2+}

Chem. - Eur. J. **2018**, *24* (2), 7702– 7709, 10.1002/chem.201800610

$4f^{n+1}\,5d^{0}$ или $4f^{n}\,5d^{1}$

Ln^{3+}/Ln^{2+} потенциалы восстановления для пары $4f^{n}/4f^{n+1}$

Для некоторых лантанидов $4f^{n}/4f^{n}5d^{1}$

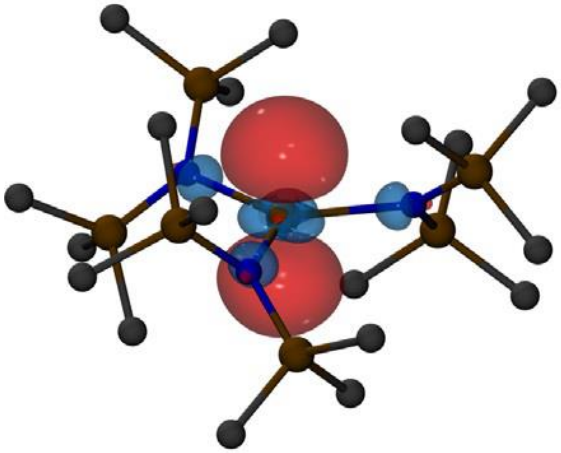


Chem. - Eur. J. **2018**, *24* (2), 7702– 7709, 10.1002/chem.201800610

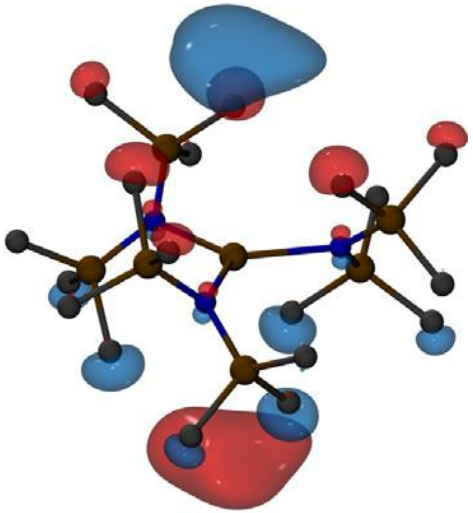
Table 1. Metrical parameters of the $[Ln(NR_2)_3]^{1-}$ anions.

Metal	Ln–N distance (Avg) [Å]	Change in Ln–N [Å] ($Ln^{3+} \rightarrow Ln^{2+}$)	$Ln–N_{Plane}$ (Avg) [Å]
Gd[a]	2.307	0.06	0.523
Tb	2.282	0.05	0.503
Dy	2.270	0.06	0.523
Ho[a]	2.256	0.04	0.509
Tm[a]	2.320	0.12	0.232

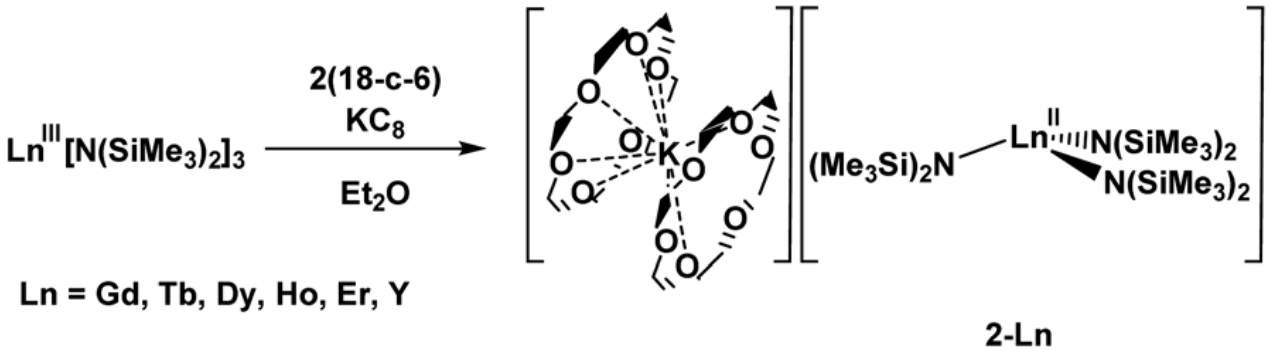
[a] These three Ln^{3+} complexes do not have reported crystal structures, so expected Ln-N distances were interpolated from analogous complexes of metals with similar ionic radii.



HOMO

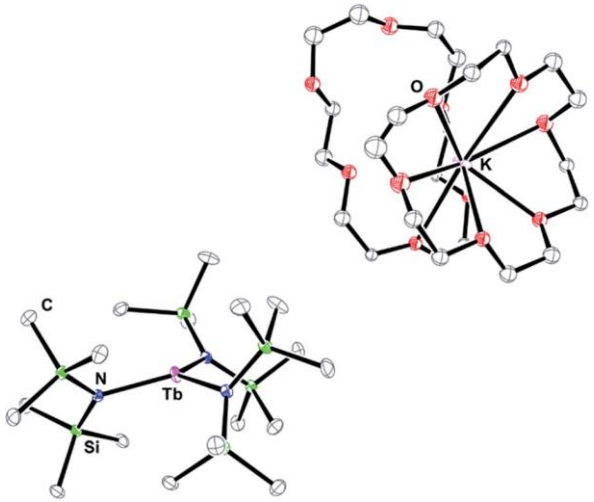


LUMO



Ln = Gd, Tb, Dy, Ho, Er, Y

2-Ln

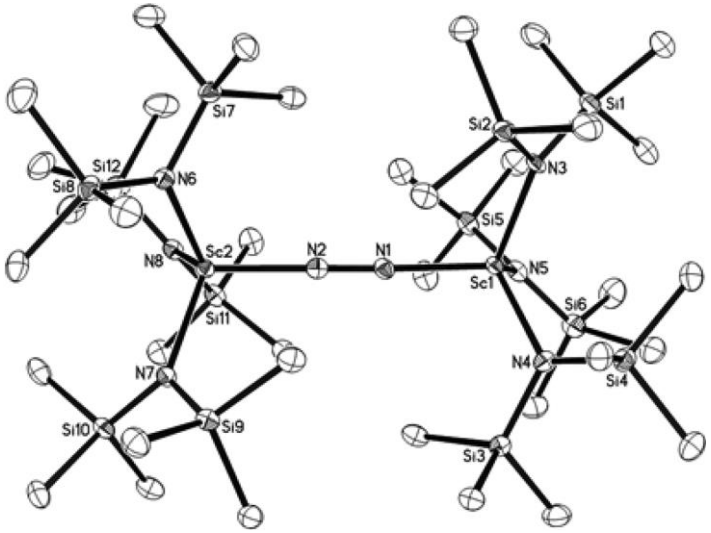


Gd, Tb, Dy, Ho, Er, Y - изоморфны

Chem. Sci. **2020**, *11* (11), 2006– 2014, DOI: 10.1039/C9SC05794C

$Sc(NR_2)_3 + KC_8 + crypt \longrightarrow$

$\{K\text{-}(crypt)\}_2\{[(R_2N)_3Sc]_2[\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2]\}$



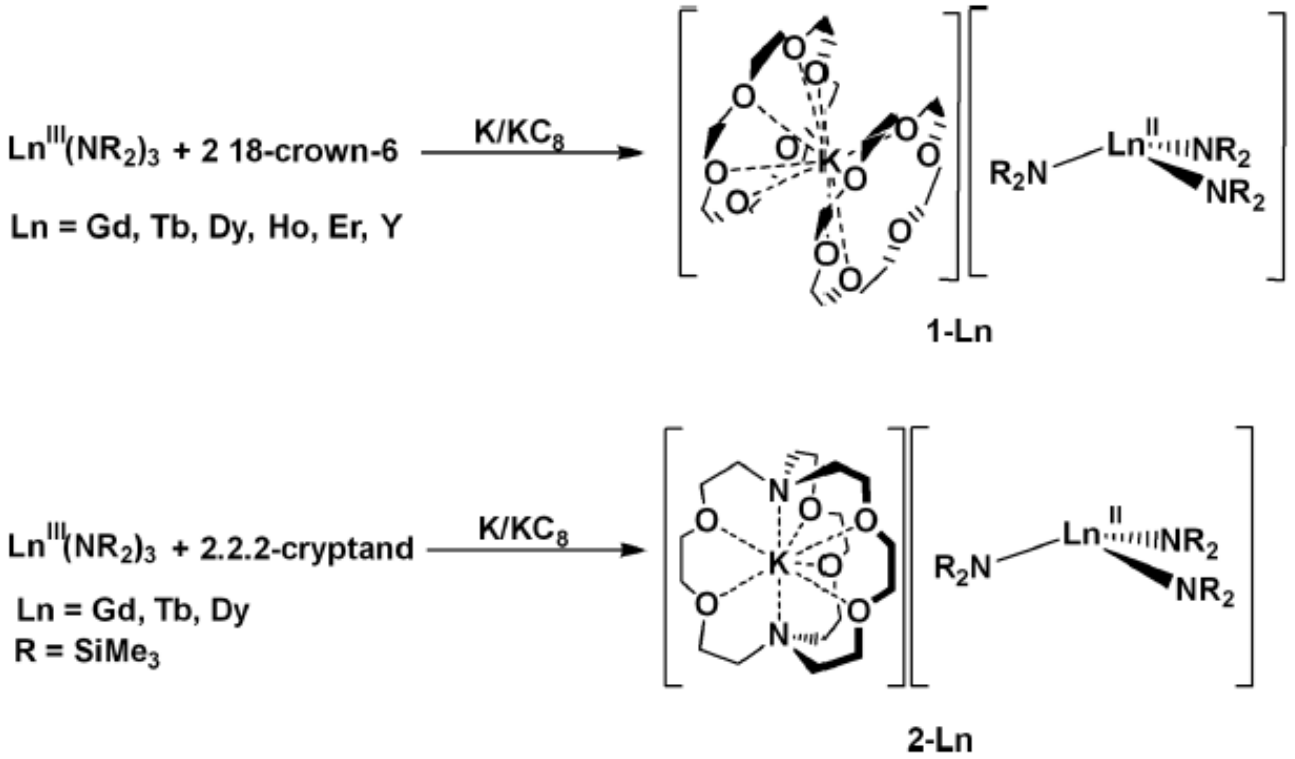
$$2\ Ln^{III}A_3 + 2\ M \xrightarrow[-\ 2\ MA]{THF,\ N_2} A_2(THF_x)Ln^{III}(\mu\text{-}N_2)Ln^{III}A_2(THF_x)$$

Ln = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu
A = NR_2, $OC_6H_3{}^tBu_2$-2,6, C_5Me_5, C_5Me_4H, $C_5H_2{}^tBu_3$
M = K, KC_8, Na; x = 0-1

$$2\ [Sc^{II}(NR_2)_3]^- \underset{hv\ -\ N_2}{\overset{+\ N_2\ -\ 35\ ^\circ C}{\rightleftharpoons}} [(R_2N)_2Sc^{III}(NR_2)\text{-}N{=}N\text{-}Sc^{III}(NR_2)_2]^{2-}$$

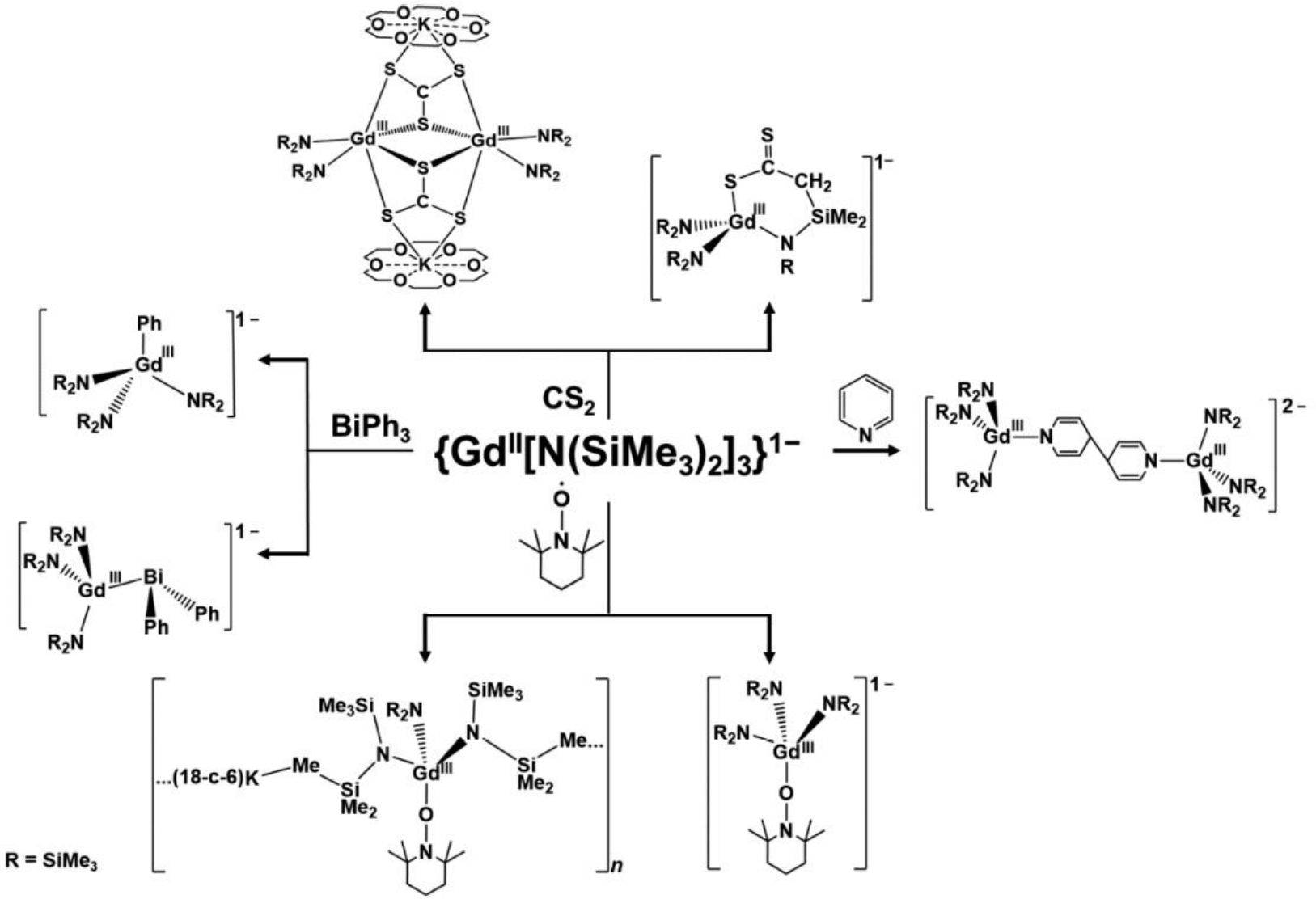
R = $SiMe_3$

J. Amer. Chem. Soc. 2017, 139, 42, 14861–14864 10.1021/jacs.7b08456



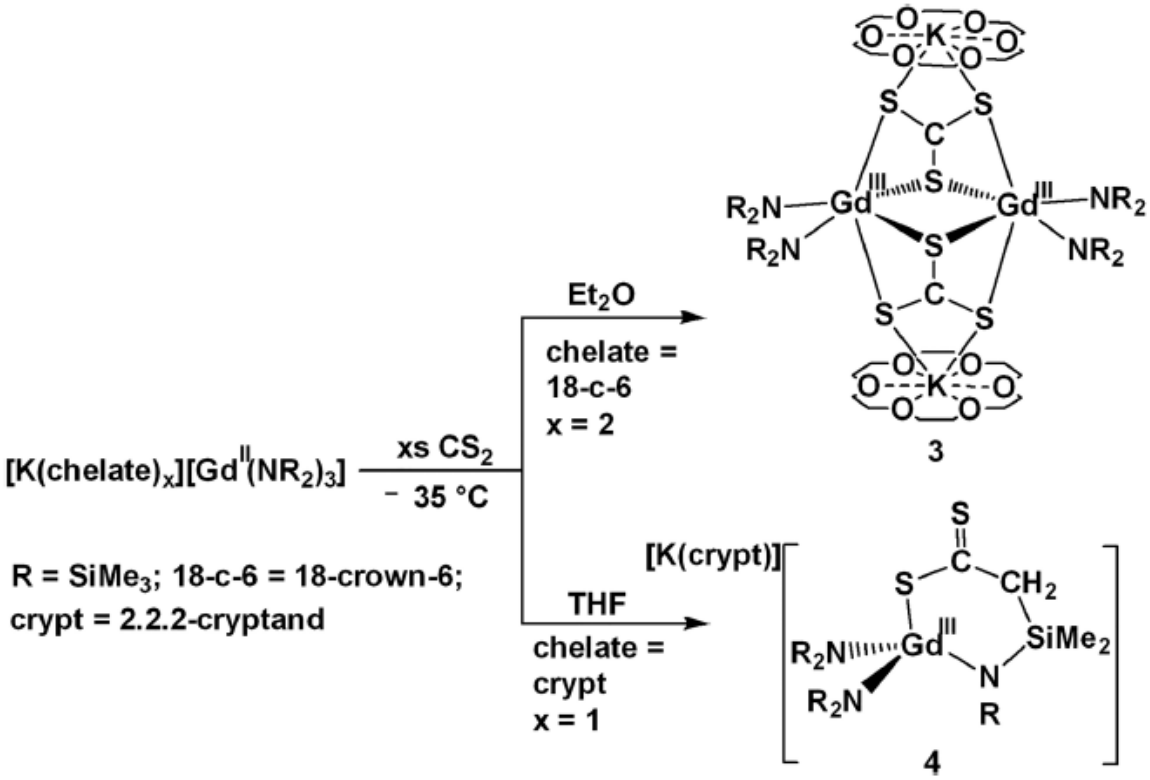
Inorg. Chem. 2021, 60, 15635−15645 [10.1021/acs.inorgchem.1c02241](https://doi.org/10.1021/acs.inorgchem.1c02241)

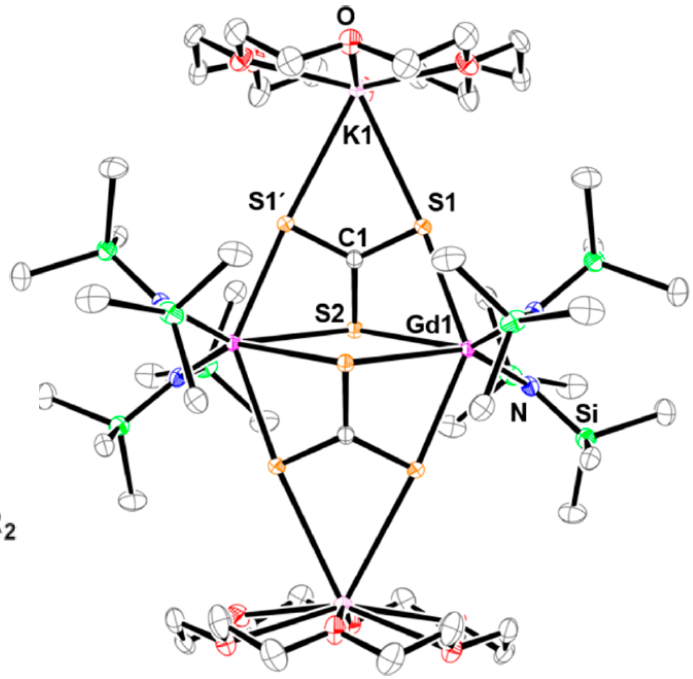
Red / Ox реакции $[Gd(N(SiMe_3)_2)_3]^-$

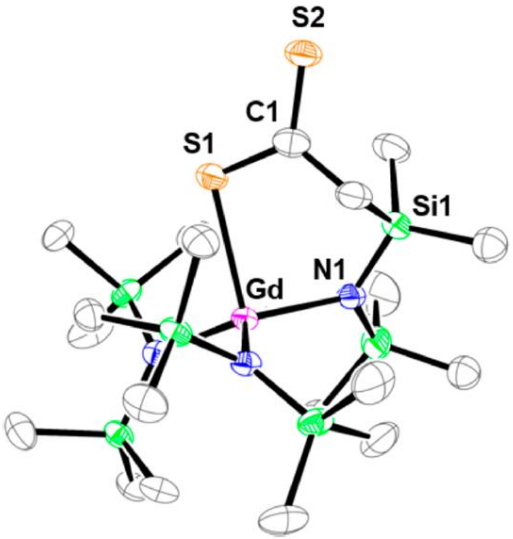


Inorg. Chem. 2021, 60, 15635−15645 10.1021/acs.inorgchem.1c02241

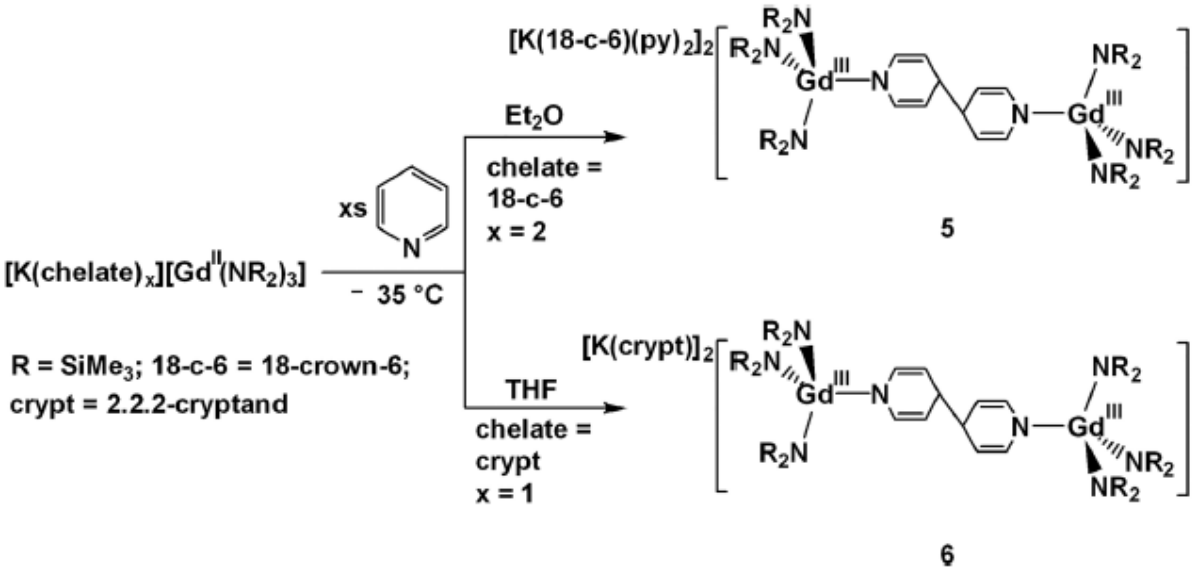
Red / Ox реакции $[Gd(N(SiMe_3)_2)_3]^-$

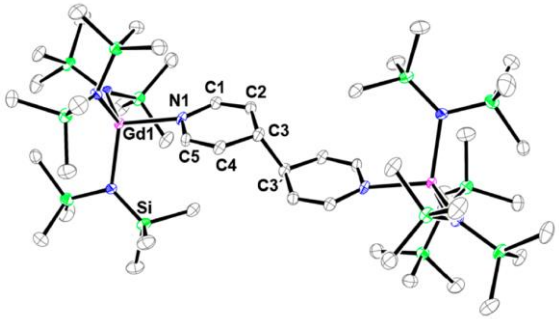




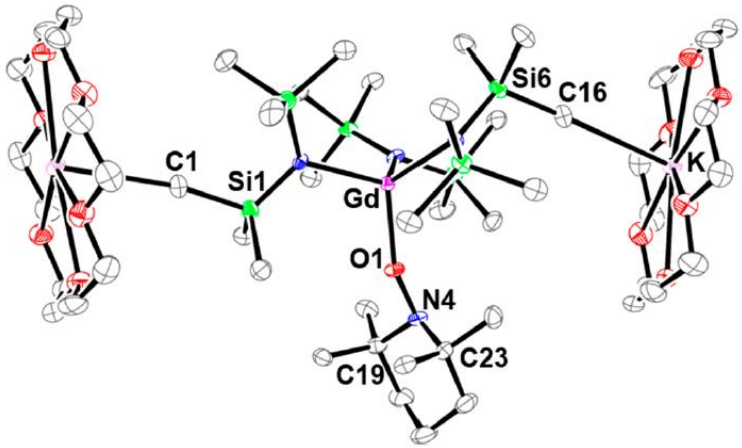


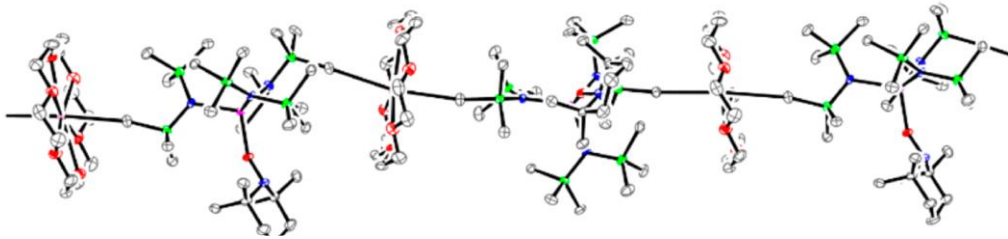
Inorg. Chem. 2021, 60, 15635−15645 10.1021/acs.inorgchem.1c02241



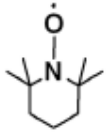


Inorg. Chem. 2021, 60, 15635−15645 [10.1021/acs.inorgchem.1c02241](https://doi.org/10.1021/acs.inorgchem.1c02241)



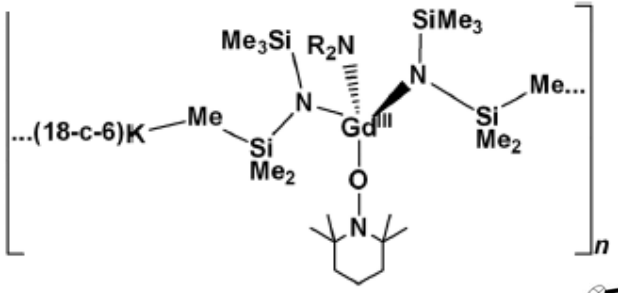


$[K(chelate)_x][Gd^{II}(NR_2)_3]$ – 35 °C



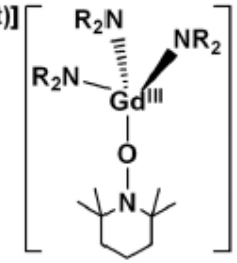
R = $SiMe_3$; 18-c-6 = 18-crown-6;
crypt = 2.2.2-cryptand

Et_2O
chelate = 18-c-6
x = 2

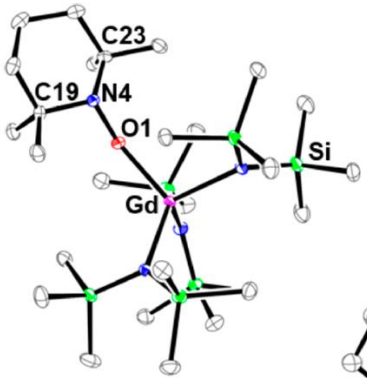


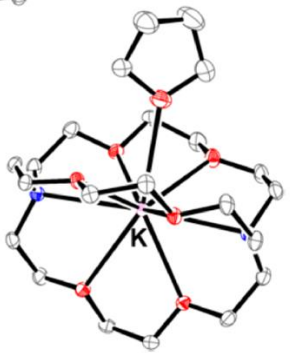
7

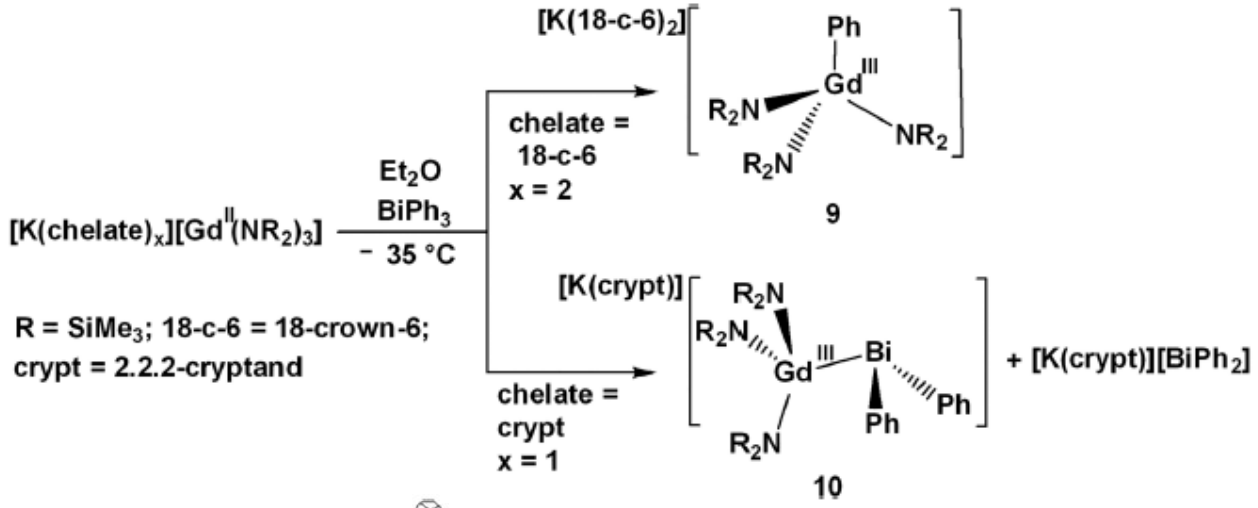
THF
chelate = crypt
x = 1

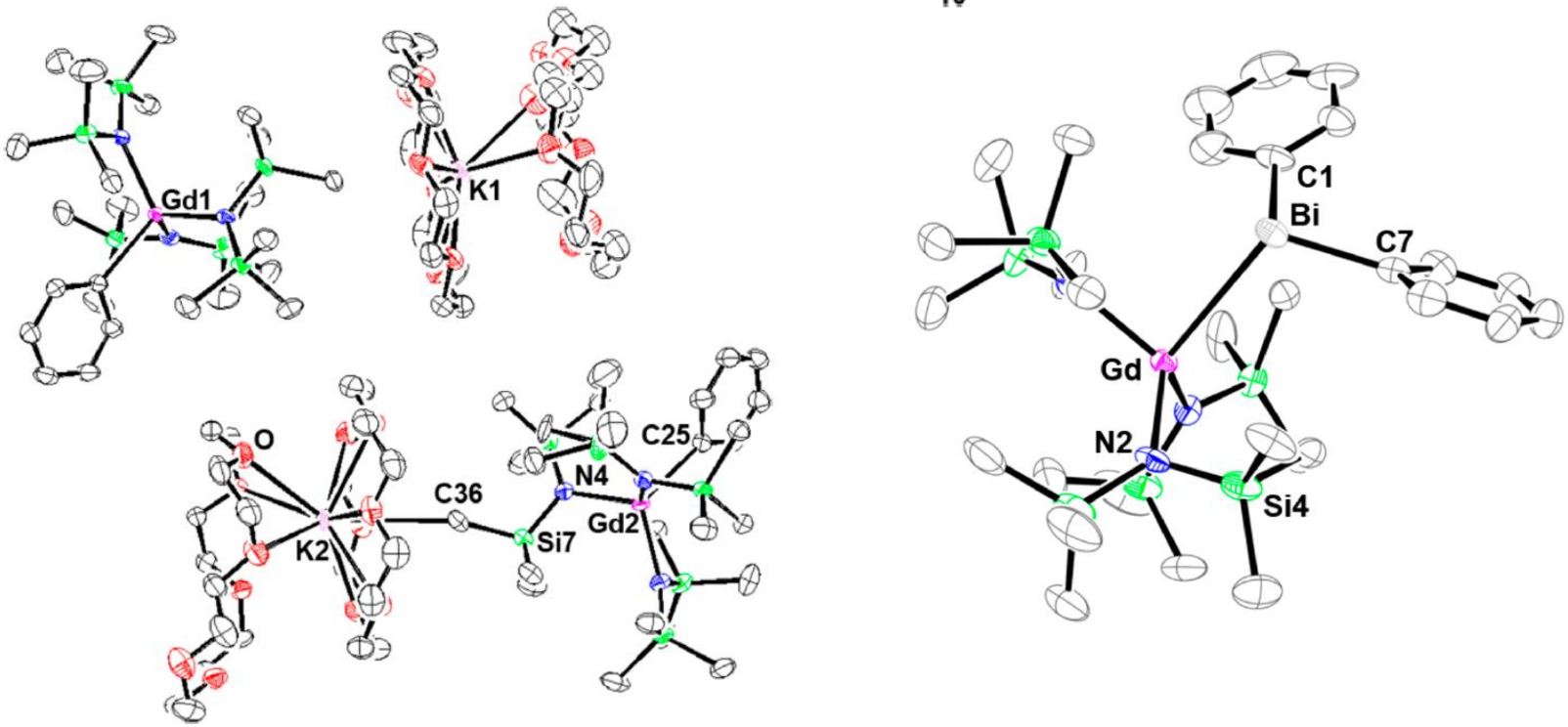


8






[K(18-c-6)2]
Ph
Gd III
R2N
NR2
R2N
chelate =
18-c-6
x = 2
9
Et2O
BiPh3
− 35 °C
[K(chelate)x][Gd II(NR2)3]
R = SiMe3; 18-c-6 = 18-crown-6;
crypt = 2.2.2-cryptand
[K(crypt)]
R2N
R2N
Gd III
Bi
Ph
Ph
R2N
+ [K(crypt)][BiPh2]
chelate =
crypt
x = 1
10


Gd1
K1
O
K2
C36
Si7
N4
Gd2
C25
C1
Bi
C7
Gd
N2
Si4

Резюме: устойчивые степени окисления

(Для молекулярных соединений Ln)

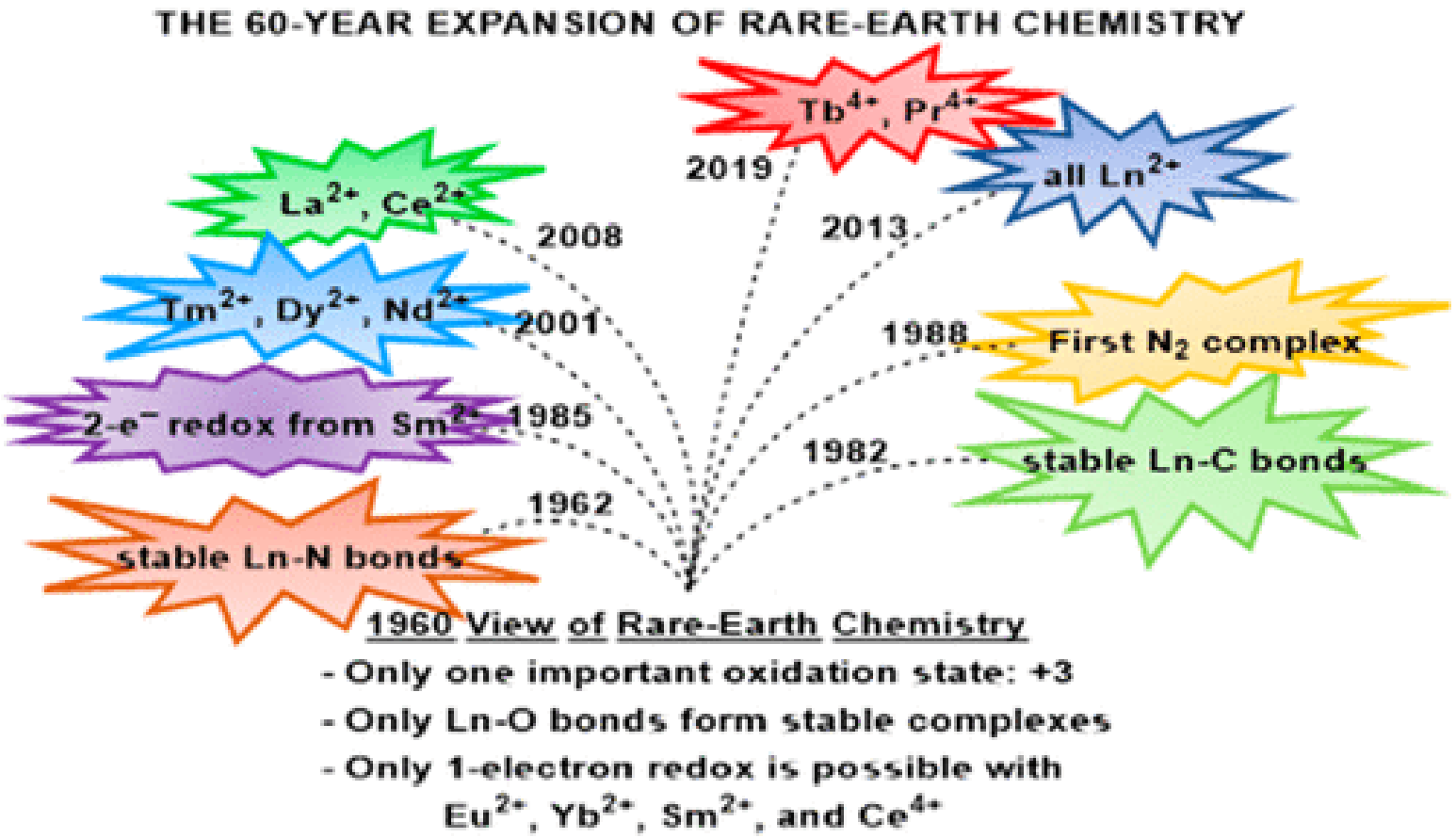
Конец XX века

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Valence Electrons	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Oxidation States	3	4 3	3	3	3	3 2	3 2	3	3	3	3	3	3	3 2	3

Начало XXI века

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Valence Electrons	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Oxidation States	3 2	4 3 2	3 2	3 2	3	3 2	3 2	3 2	3 2	3 2	3 2	3 2	3 2	3 2	3 2

Эпилог



J.Am.Chem.Soc. **2021**, 143, 18354–18367 10.1021/jacs.1c08288