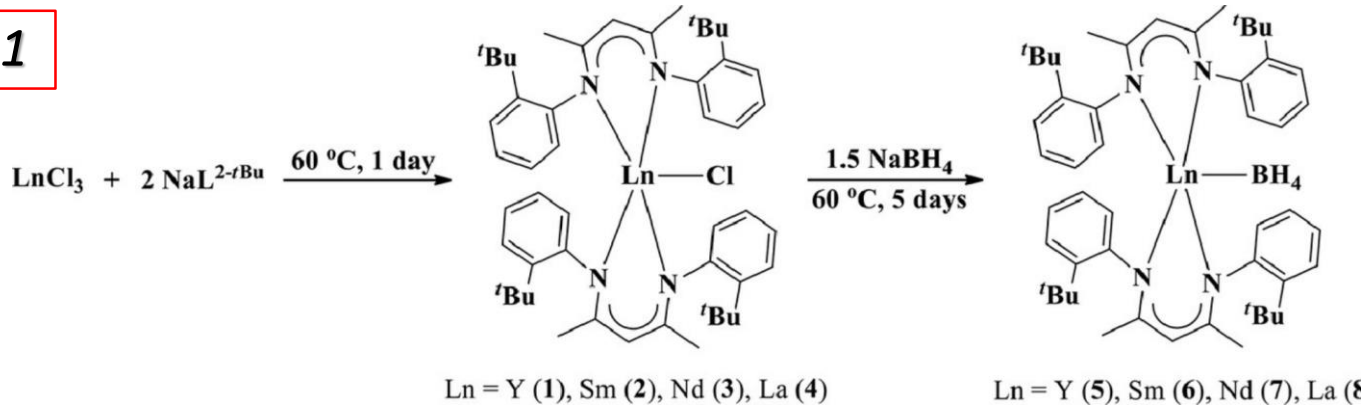
Боргидридные комплексы РЗЭ начала 4-f ряда

Садртдинова без Г.И. на сайте

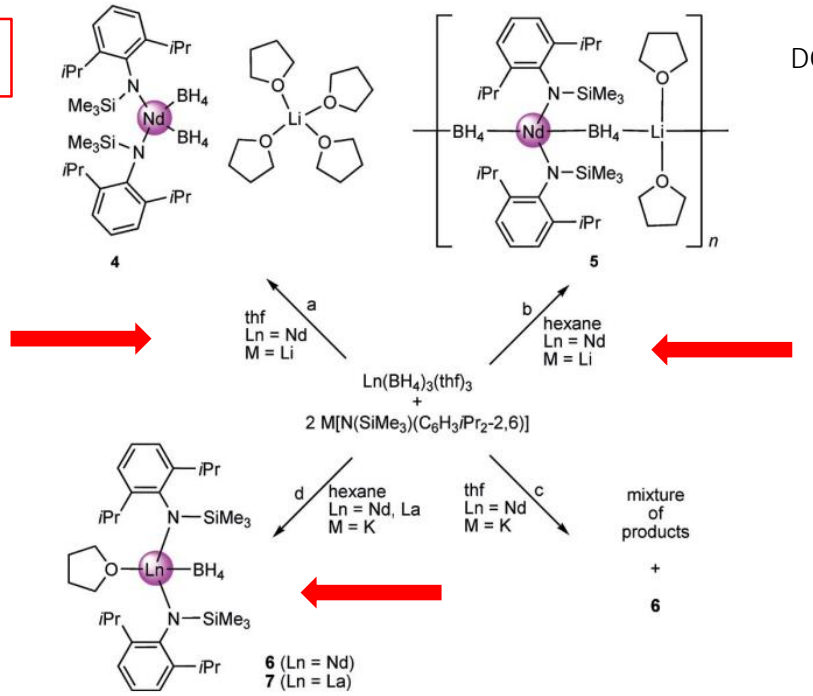
Методы синтеза боргидридных комплексов

1



https://doi.org/10.1016/j.jorganchem.2020.121662

2

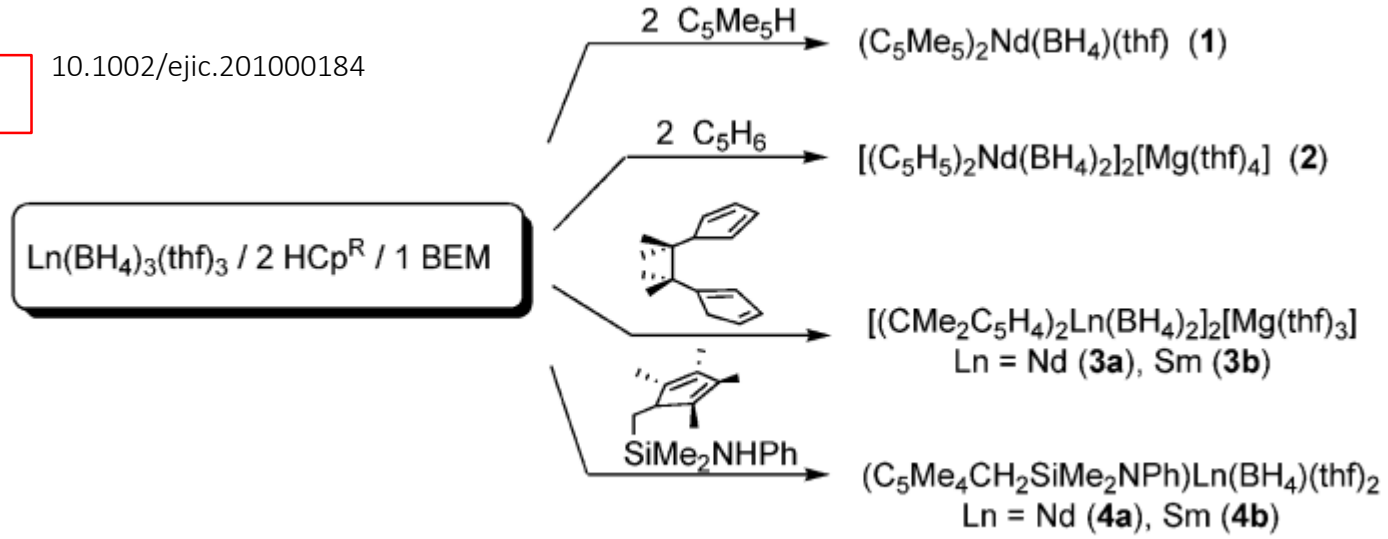


DOI: 10.1002/ejic.201000220

Методы синтеза боргидридных комплексов

3

10.1002/ejic.201000184



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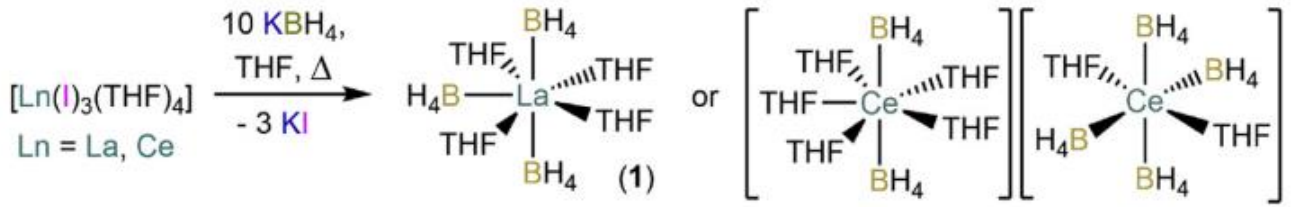
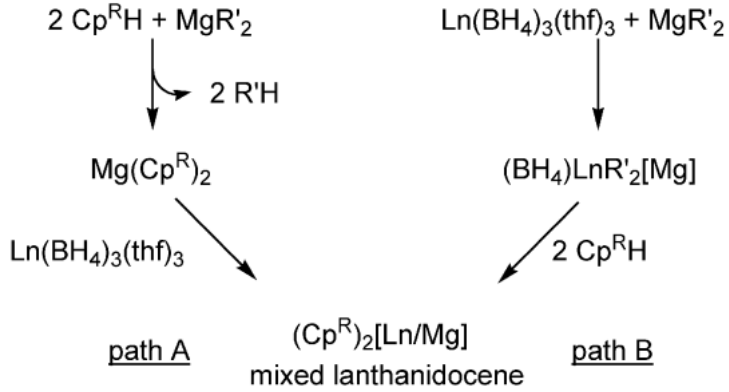
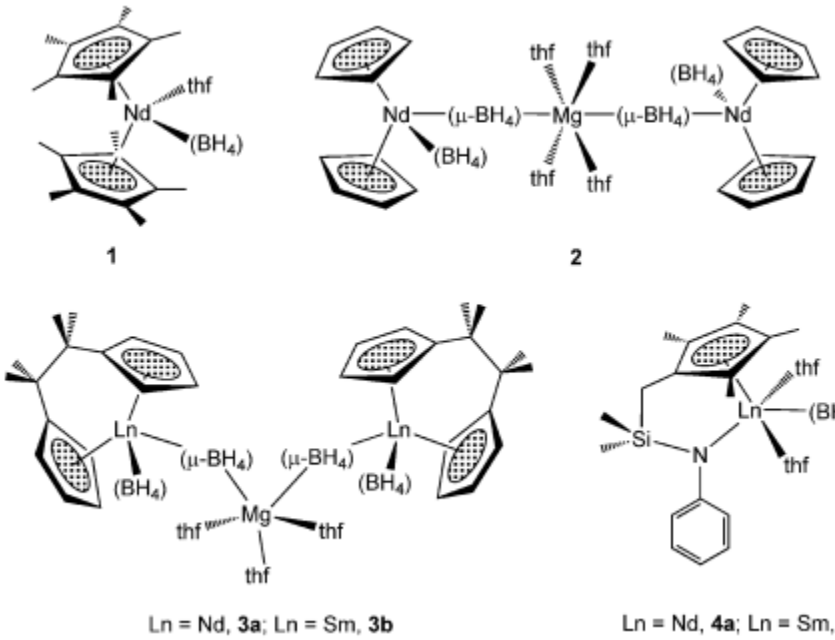


Scheme 1. Synthesis of $[Ln(BH_4)_3(THF)_n]$ [Ln = La, n = 4 (**1**); Ln = Ce, n = 3.5].

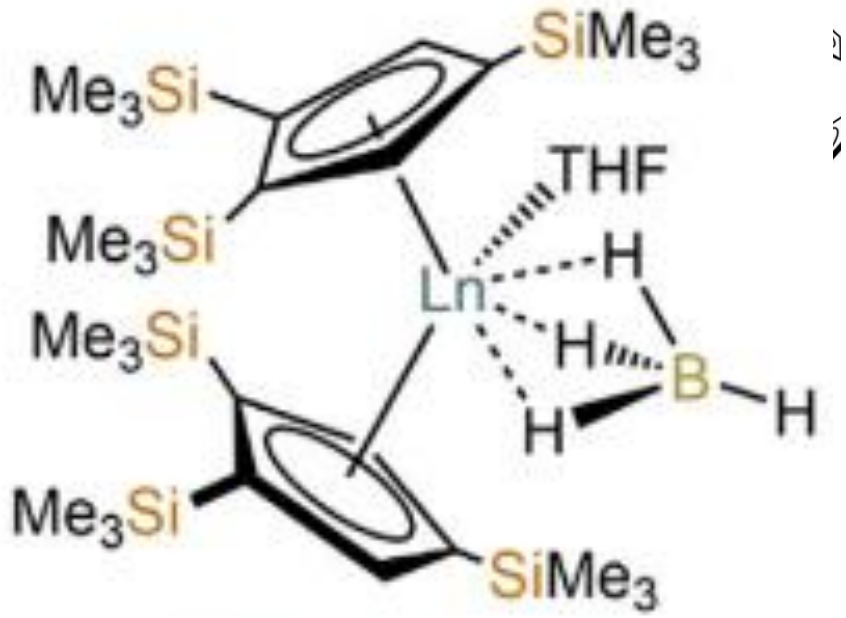
https://doi.org/10.1016/j.jorganchem.2017.09.010

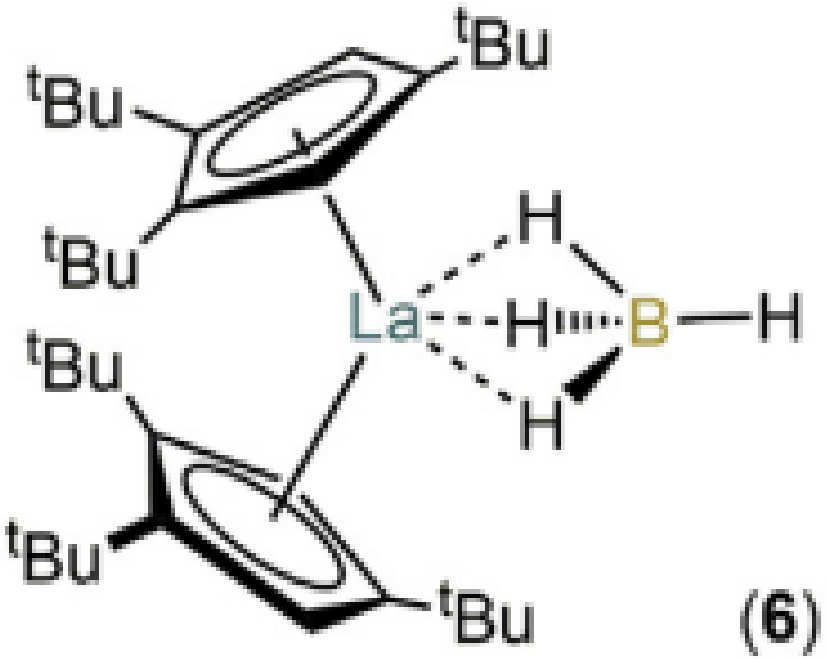




Разные типы координации боргидрида

2





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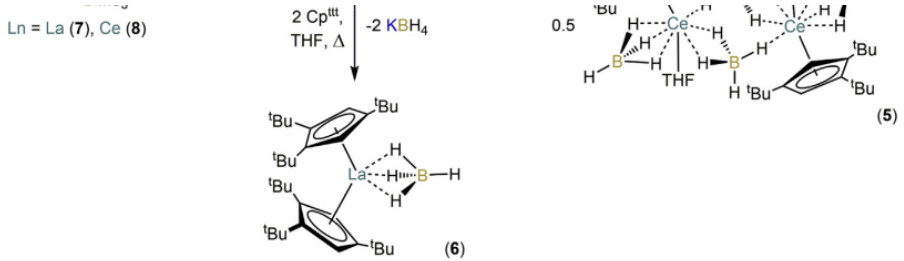


Scheme 2. Synthesis of **2**–**3** and **5**–**8** from KCp^R ($Cp^R = Cp^{tt}$, Cp^{ttt}, Cp''') and **1** or $[Ce(BH_4)_3(THF)_{3.5}]$.

https://doi.org/10.1016/j.jorganchem.2017.09.010

Разные типы координации боргидрида

3

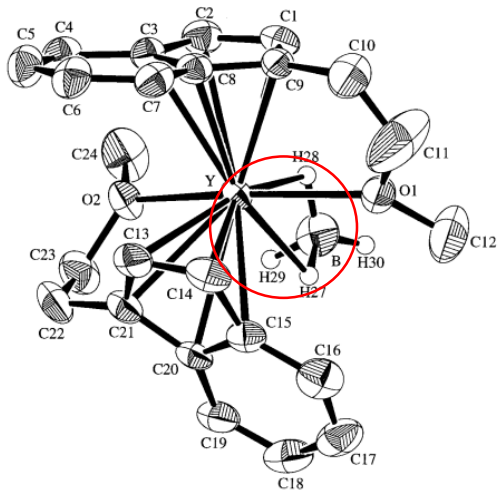
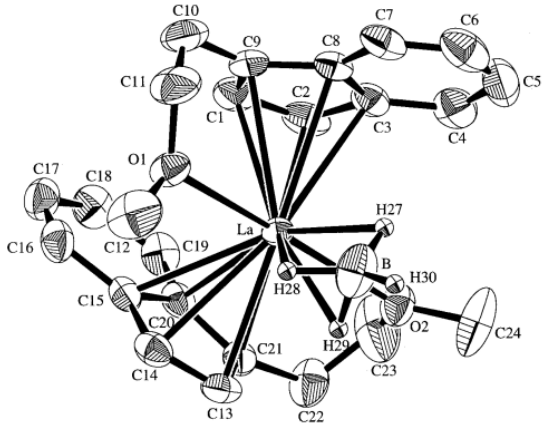


Fig. 1. Molecular structure of complex **1**.



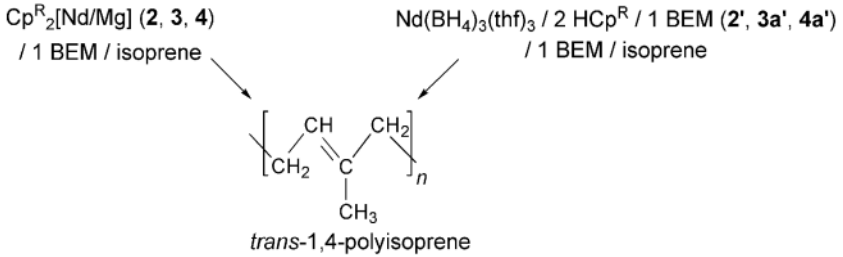
$$(MeOCH_2CH_2C_9H_6)_2LnCl + NaBH_4 \xrightarrow[\text{r.t./48 h}]{\text{THF}} (MeOCH_2CH_2C_9H_6)_2LnBH_4 + NaCl$$

$$Ln = Y(\mathbf{1})\ 85\%,\ La(\mathbf{2})\ 81\% \qquad (1)$$

Катализ

Изопрен

1



trans-1,4-polyisoprene

10.1002/ejic.201000184

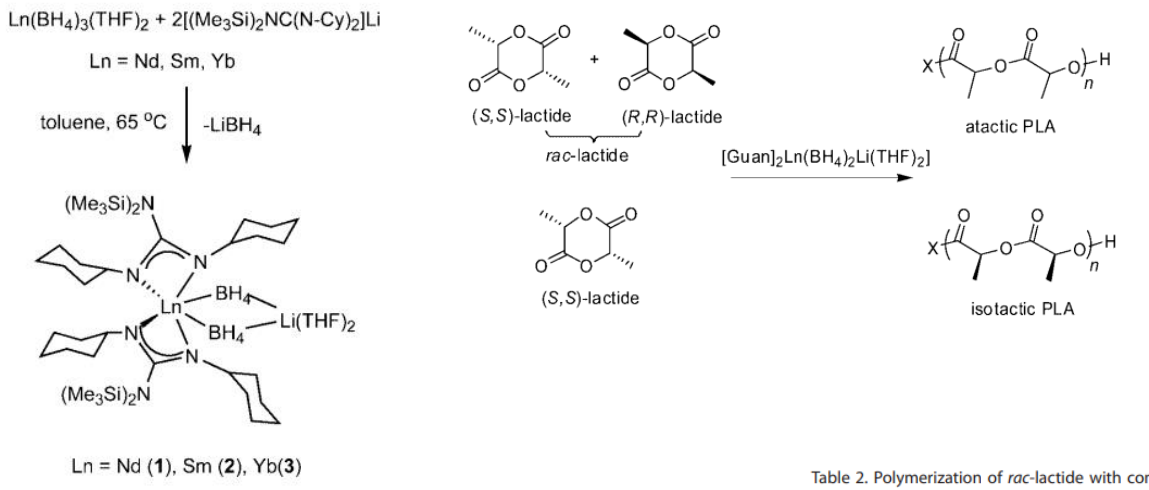
Run[a]	Precatalyst	Yield [%]	*trans*-1,4 [%][b]	3,4 [%]	M_n(exp.)$\times 10^{-3}$ [g mol^{-1}][c]	PDI[d]
1	**2**	18	90.0	9.0	21.3	1.80
2	**2′**	27	81.2	8.0	15.0	1.40
3	**3a**	72	92.5	6.5	9.9	2.12
4	**3a′**	83	93.1	5.9	12.1	1.76
5	**4a**	83	85.2	14.5	8.4	1.73
6	**4a′**	82	84.9	14.3	17.5	1.57

[a] Experimental conditions: V(isoprene) = V(toluene) = 1 mL, [isoprene]/[Nd] = 1000, [BEM]/[Nd] = 1, T = 50 °C, t = 72 h. [b] Determined by ^{1}H and ^{13}C NMR spectroscopy, residual proportion = *cis*-1,4 defects. [c] Determined by size exclusion chromatography (SEC), with a correction factor of 0.5.[33] [d] Polydispersity index M_w/M_n.

Катализ

Лактид

1



Ln = Nd (**1**), Sm (**2**), Yb(**3**)

Table 3. Polymerization of *rac*- and (*S*,*S*)-lactide with complexes **1**–**3**.[a]

Entry	M	Complex	[M]/[Ln]	Solvent	Time[b] [min]	Conv.[c] [mol-%]	$M_{n,th}$[d] [g/mol]	$M_{n,exp}$[e] [g/mol]	M_w/M_n[e]
1	*rac*-LA	**1**	100	toluene	17	>98	14100	16500	1.98
2	*rac*-LA	**1**	200	toluene	10	62	17900	20800	1.68
3	*rac*-LA	**1**	200	toluene	30	>98	25900	26300	1.51
4	*rac*-LA	**1**	400	toluene	60	>98	51800	52000	1.09
5	*rac*-LA	**1**	100	THF	60	97	8400	6500	2.16
6	(*S*,*S*)-LA	**1**	200	THF	20	30	8600	6000	1.44
7	(*S*,*S*)-LA	**1**	200	THF	60	98	28200	17300	1.63
8	*rac*-LA	**2**	100	toluene	300	95	13700	9100	1.50
9	*rac*-LA	**2**	200	toluene	480	96	27600	23500	1.16
10	*rac*-LA	**2**	400	toluene	1000	95	54700	20100	2.73
11	(*S*,*S*)-LA	**2**	200	THF	60	12	3400	2200	1.56
12	*rac*-LA	**2**	200	THF	1000	98	28200	9400	2.99
13	*rac*-LA	**3**	100	toluene	150	95	13700	11100	1.24
14	*rac*-LA	**3**	200	toluene	270	95	27400	15500	1.77
15	*rac*-LA	**3**	400	toluene	1000	94	54100	25000	2.17

[a] General conditions: [LA] = 0.5 mol/L, T = 20 °C. [b] Reaction time was not necessarily optimized. [c] Conversion of monomer M as determined by ^{1}H NMR spectroscopy. [d] M_n value calculated assuming one polymer chain per metal center, from the relation: 144 × conv × [M]/[Ln]. [e] Experimental (corrected; see Exp. Sect.) M_n and M_w/M_n values determined by GPC in THF vs. polystyrene standards.

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2

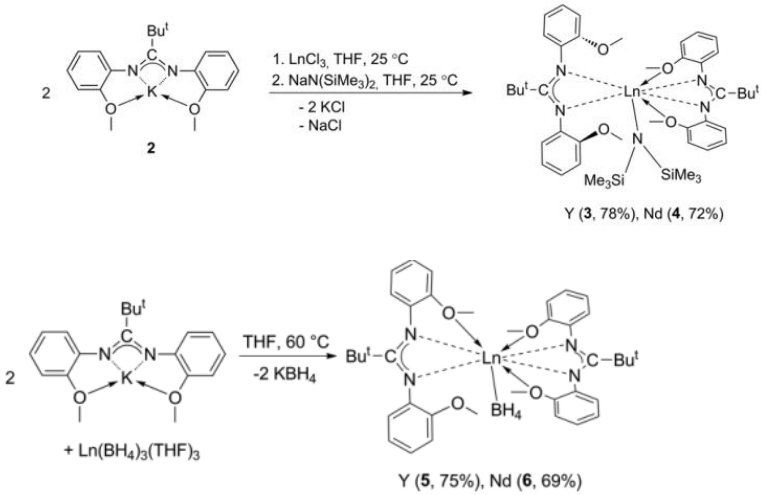


Table 2. Polymerization of *rac*-lactide with complexes **3**–**6**.[a,b]

№	Cat	$[M]_0/[Ln]_0$	t/min[c]	M_{ncalc} ×10^{-3}	M_{nexp}×10^{-3}	M_w/M_n[d]	P_r
1	3	100:1	70	14.4	28.7	1.6	0.53
2	**3**	250:1	140	36.0	33.3	1.4	0.53
3	**3**	500:1	270	72.0	76.0	1.7	0.54
4	5	100:1	15	14.4	12.1	2.5	0.53
5	**5**	250:1	25	36.0	31.4	1.9	0.52
6	**5**	500:1	35	72.0	64.9	2.1	0.53
7	**3**/^{i}PrOH	100:1	60	14.4	7.8	2.2	0.53
8	**3**/^{i}PrOH	250:1	120	36.0	14.7	1.7	0.52
9	**3**/^{i}PrOH	500:1	240	72.0	30.1	1.7	0.53
10	**3**/^{t}BuOH	250:1	150	36.0	6.8	3.5	0.53
11	**3**/PhOH	250:1	180	36.0	14.4	2.9	0.52
12	**4**	100:1	60	14.4	15.0	2.2	0.54
13	**4**	250:1	90	36.0	48.2	1.4	0.53
14	**4**	500:1	150	72.0	68.9	1.9	0.54
15	**6**	100:1	10	14.4	8.2	1.9	0.53
16	**6**	250:1	15	36.0	22.9	2.4	0.52
17	**6**	500:1	20	72.0	52.2	1.4	0.53
18	**4**/^{i}PrOH	100:1	40	14.4	8.9	2.0	0.53
19	**4**/^{i}PrOH	250:1	60	36.0	14.9	1.6	0.52
20	**4**/^{i}PrOH	500:1	120	72.0	39.3	1.4	0.53

[a] General conditions: toluene, [M] = 1.0 mol/L, T = 25 °C. [b] The conversion of the monomer M was determined by ^{1}H NMR spectroscopy and is quantitative in all experiments. [c] Reactions times were not optimized. [d] Experimental (corrected; see Experimental Section) M_n and M_w/M_n values determined by GPC in THF vs. PS standards and corrected with a factor of 0.58. M_n value calculated by assuming one polymer chain per metal center with the relationship: 144.14 × conversion × [M]/[Ln].

10.1002/ejic.201900897

Катализ

10.1002/ejic.201900897

Капролактон

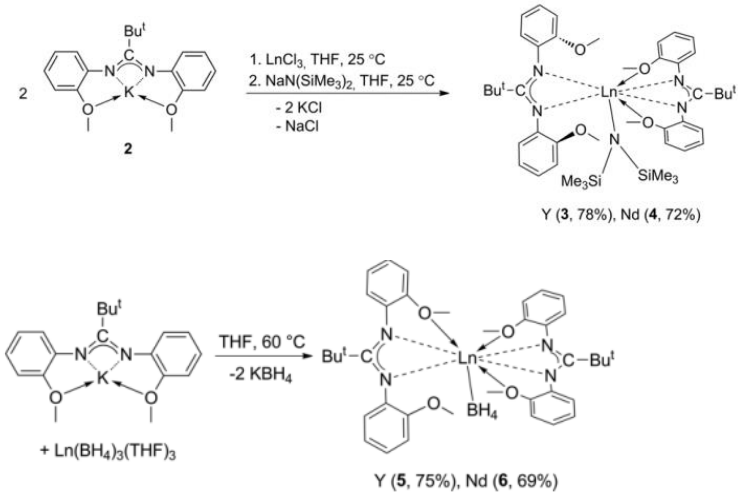


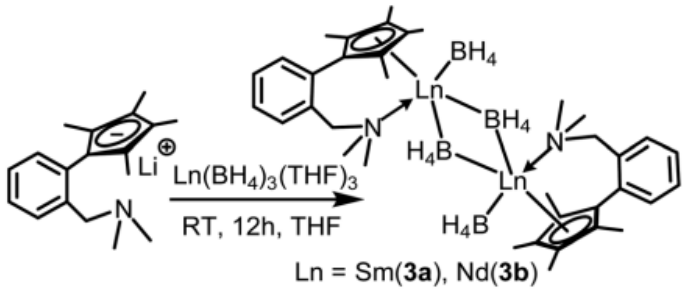
Table 3. Polymerization of ε-caprolactone with complexes **3**–**6**.[a,b]

№	Cat	$[M]_0/[Ln]_0$	t/s[c]	M_{ncalc}	M_{nexp}	M_w/M_n[d]
				$\times10^{-3}$	$\times10^{-3}$	
1	3	100:1	30	11.4	58.4	2.6
2	**3**	250:1	60	28.5	85.0	2.4
3	**3**	500:1	120	57.1	243.8	2.1
4	5	100:1	60	11.4	8.4	1.7
5	**5**	250:1	150	28.5	26.1	2.0
6	**5**	500:1	400	57.1	48.0	2.0
7	**3**/Pr^iOH	100:1	10	11.4	7.5	2.4
8	**3**/Pr^iOH	250:1	30	28.5	18.5	2.1
9	**3**/Pr^iOH	500:1	60	57.1	26.8	1.6
10	**3**/Bu^tOH	500:1	25	57.1	36.0	3.2
11	**3**/PhOH	500:1	120	57.1	8.8	2.6
12	**4**	100:1	20	11.4	78.3	2.2
13	**4**	250:1	30	28.5	233.5	1.7
14	**4**	500:1	60	57.1	271.5	1.6
15	**6**	100:1	20	11.4	10.7	1.5
16	**6**	250:1	30	28.5	29.5	1.8
17	**6**	500:1	40	57.1	53.3	1.6
18	**4**/Pr^iOH	100:1	10	11.4	34.1	1.7
19	**4**/Pr^iOH	250:1	25	28.5	44.7	1.3
20	**4**/Pr^iOH	500:1	50	57.1	54.9	1.4

[a] General conditions: toluene, [M] = 1.0 mol/L, T = 25 °C. [b] The conversion of the monomer M was determined by ^{1}H NMR spectroscopy and is quantitative in all experiments. [c] Reactions times were not optimized. [d] Experimental (corrected; see Experimental Section) M_n and M_w/M_n values determined by GPC in THF vs. PS standards and corrected with a factor of 0.56. M_n value calculated by assuming one polymer chain per metal center with the relationship: 114.14 × conversion × [M]/[Ln].

Катализ

Метилметакрилат



10.1039/c9dt04029c

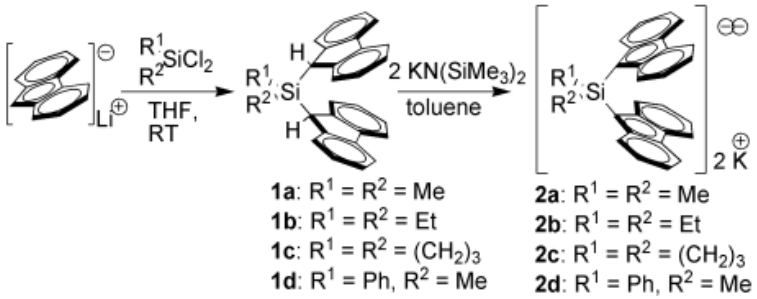
Entry	Cat.	Co-cat.	Solvent	T (°C)	t (min)	Conv.[b] (%)	M_n[c] ($\times 10^4$)	M_w/M_n[c]	Tacticity[d] (%) mm-mr-rr
1	**3a**	—	—	20	10	79.2	1.23	2.35	24-41-35
2	**3b**	—	—	20	10	58.0	1.33	3.12	51-28-21
3	**3a**	—	Tol	20	240	9.3	1.03	1.87	51-35-14
4	**3a**	—	Tol	0	240	34.5	1.77	2.79	51-31-18
5	**3b**	—	Tol	20	240	5.7	1.06	1.78	60-31-9
6	**3b**	—	Tol	0	240	28.4	2.00	3.96	56-32-12
7	**3a**	—	THF	20	30	69.6	3.30	2.03	6-32-62
8	**3b**	—	THF	20	240	77.6	1.36	1.79	6-34-60
9[e]	**3b**	—	THF	20	240	72.6	1.54	1.84	7-38-55
10[f]	**3b**	—	THF	20	240	57.4	1.61	1.77	12-39-48
11	**3a**	^{n}BuLi	Tol	20	30	13.1	1.02	1.73	60-32-8
12	**3a**	^{n}BuLi	THF	20	30	71.4	1.11	1.82	6-36-58
13	**3a**	^{n}BuLi	THF	0	30	60.0	2.93	1.94	6-31-63
14	**3a**	^{n}BuLi	THF	−20	15	73.1	4.99	1.86	3-26-71
15	**3a**	^{n}BuLi	THF	−40	5	76.3	7.52	2.44	3-24-73
16	**3b**	^{n}BuLi	THF	20	90	61.2	1.24	1.75	7-36-57
17	**3b**	^{n}BuLi	THF	0	60	81.8	2.42	1.83	6-32-62
18	**3b**	^{n}BuLi	THF	−20	30	72.7	5.34	3.56	4-29-67
19	**3b**	^{n}BuLi	THF	−40	30	77.8	5.75	2.14	4-28-68
20	**3a**	Me_3SiCH_2Li	THF	20	30	70.6	1.22	1.88	7-32-61
21	**3a**	MeLi	THF	20	30	71.8	1.13	1.93	5-35-60
22	**3a**	^{i}PrMgBr	THF	20	30	70.2	1.28	2.01	5-34-61
23	**3a**	^{n}BuLi	Et_2O	20	30	62.6	1.26	1.70	8-37-55
24	**3a**	^{n}BuLi	Dioxane	20	30	71.1	1.29	1.86	6-34-60

[a] Conditions: Cat. (10 μmol), solvent (1 mL), [MMA]/[Cat.] = 500, [^{n}BuLi]/[Cat.] = 3. [b] Conversion = weight of polymer obtained/weight of monomer used. [c] Determined by GPC calibrated with the standard polystyrene samples. [d] Determined by ^{1}H NMR spectroscopy in $CDCl_3$ (mm: isotactic triad rate; mr: atactic triad rate; and rr: syndiotactic triad rate). [e] [MMA]/[Cat.] = 800. [f] [MMA]/[Cat.] = 1000.

Катализ

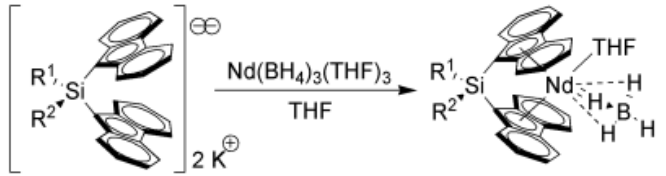
10.1039/c0nj00274g

Сополимеризация
бутадиен-этилен



1a: $R^1 = R^2 = Me$
1b: $R^1 = R^2 = Et$
1c: $R^1 = R^2 = (CH_2)_3$
1d: $R^1 = Ph$, $R^2 = Me$

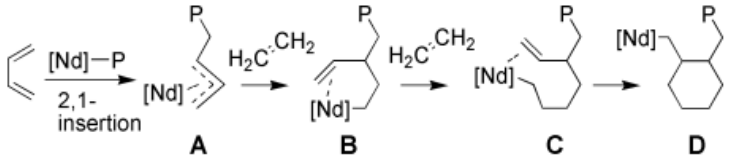
2a: $R^1 = R^2 = Me$
2b: $R^1 = R^2 = Et$
2c: $R^1 = R^2 = (CH_2)_3$
2d: $R^1 = Ph$, $R^2 = Me$



2a: $R^1 = R^2 = Me$
2b: $R^1 = R^2 = Et$
2c: $R^1 = R^2 = (CH_2)_3$
2d: $R^1 = Ph$, $R^2 = Me$

3a: $R^1 = R^2 = Me$
3b: $R^1 = R^2 = Et$
3c: $R^1 = R^2 = (CH_2)_3$
3d: $R^1 = Ph$, $R^2 = Me$

$\{(Me_2SiFlu_2)Nd(\mu\text{-}BH_4)[(\mu\text{-}BH_4)Li(THF)]\}_2$ **(4)**

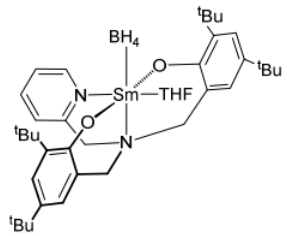


Run	Compd.	Butadiene in feed (mol%)	*n*(Nd) (μmol)	Yield (g)	Time (min)	M_n (PDI)[c] (g mol^{-1})	Activity (kg mol^{-1} h^{-1})
1[b]	**4**	30	20.0	7.5	180	33 300 (1.68)	123.0
2	**3a**	30	20.0	7.19	180	32 000 (1.8)	119.8
3	**3b**	30	19.5	6.43	173	24 200 (1.86)	114.4
4	**3c**	30	18.7	5.67	171	21 400 (3.44)	106.4
5	**3d**	30	21.0	6.33	180	33 100 (1.82)	100.5
6	**3b**	15	16.8	8.84	180	25 900 (1.65)	175.4
7	**3c**	15	22.0	7.27	114	36 700 (4.10)	173.9
8	**3d**	15	19.6	7.87	180	20 100 (1.73)	133.8
9	**3d**	60	19.5	2.42	180	11 400 (3.88)	41.4

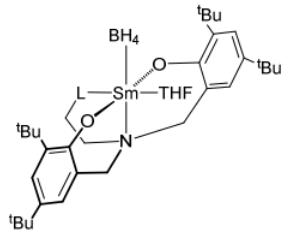
[a] Polymerisation conditions : toluene (200 mL), BoMag 0.2 mmol ([Mg]/[Nd] = 10), 80 °C, 4 bar. [b] According to ref. 7. [c] M_n: number-average molecular weight; PDI: polydispersity index.

Катализ

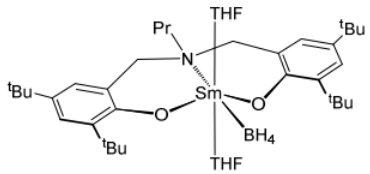
Стирол



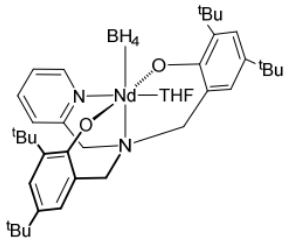
$Sm(O_2N^{Py})(BH_4)(THF)$ (**1-Sm**)



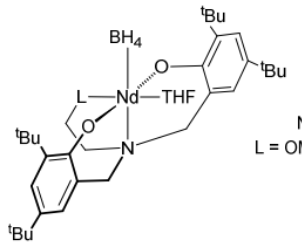
$Sm(O_2N^{L})(BH_4)(THF)$
L = OMe (**2-Sm**) or NMe_2 (**3-Sm**)



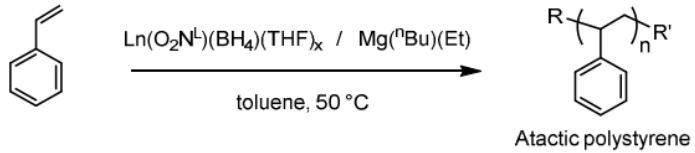
$Sm(O_2N^{Pr})(BH_4)(THF)_2$ (**4-Sm**)



$Nd(O_2N^{Py})(BH_4)(THF)$ (**1-Nd**)



$Nd(O_2N^{L})(BH_4)(THF)$
L = OMe (**2-Nd**) or NMe_2 (**3-Nd**)

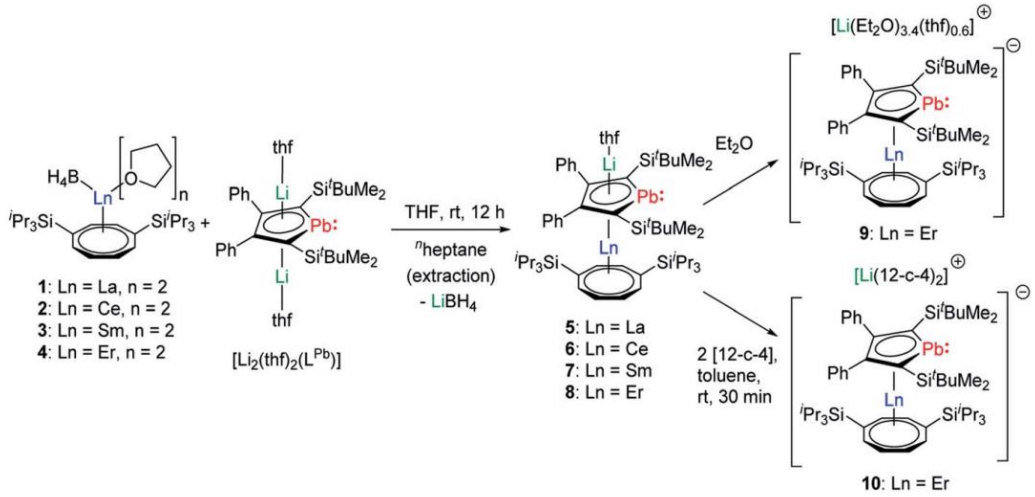


Run	Complex	Time	Yield (%) [b]	M_n (SEC) [c]	M_n (theo) [d]	$Đ$ [c]
8	**1-Sm**	90 min	6	5200	3280	1.81
9	**2-Sm**	90 min	88	30700	48100	1.73
10	**3-Sm**	90 min	88	22200	48100	1.81
11 [e]	**4-Sm**	90 min	73	34800	47500	1.58
12	**1-Nd**	20 h	13	3400	7100	1.77
13	**2-Nd**	20 h	79	6650	43200	2.08
14	**3-Nd**	20 h	56	9100	30620	1.75

[a] Experimental conditions: T = 50 °C; [Mg]/[Ln] = 1; [ST]/[Ln] = 1050, n[Ln] = 6.2×10^{-6} mol ; V(ST) = 0.75 ml; solvent = toluene with V(toluene) = 0.25 mL. [b] Isolated yield. [c] Determined by SEC in THF at 40°C against polystyrene standards, $Đ = M_w / M_n$. [d] Calculated M_n = [ST]/[Ln] × 104.15 × isolated yield, calculated for two growing chains per Mg. [e] [ST]/[Ln] = 1250.

10.1039/C5DT00252D

Приколы



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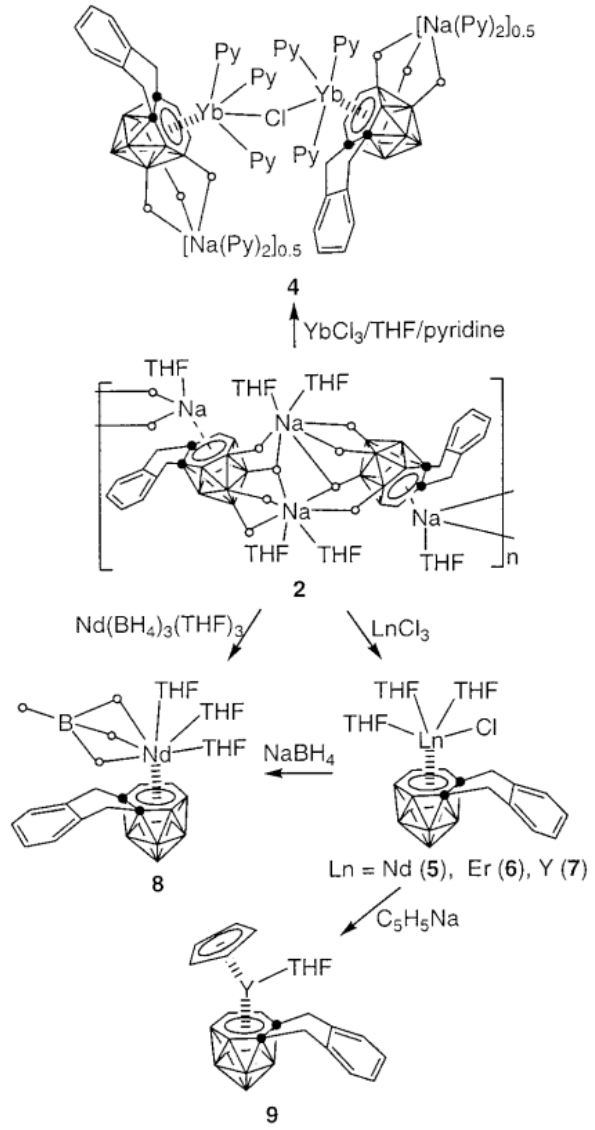

10.1021/om020299p

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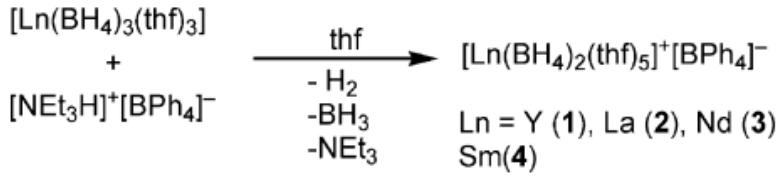
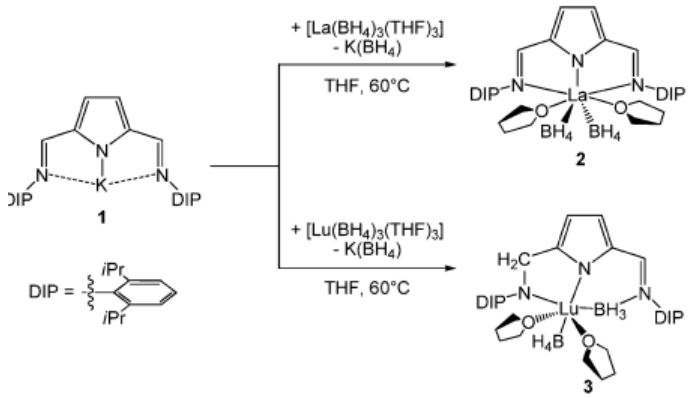


Scheme 1 Formation of $[Ln(BH_4)_2(thf)_5]^+[BPh_4]^-$. Conditions: 25 °C, 2 h. Yields: 85% (**1**), 67% (**2**), 81% (**3**), 84% (**4**).

10.1039/b801030g



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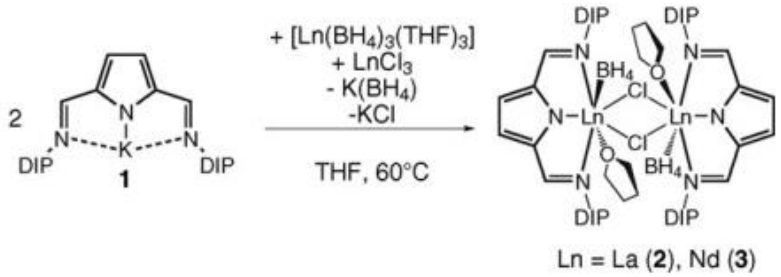

10.1016/j.crci.2009.11.003