Complexes of Group 3 Metals and Lanthanides That Contain Siloxane-Bridged Bisaminopyridinato Ligands: Synthesis, Structure, and Application in the Ring-Opening Polymerization of Lactones

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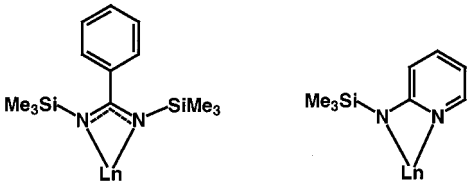
The reaction of one equivalent of dilithiated $O(SiMe_2\text{-}Ap\text{-}H)_2$ [Ap-H = -N(2-amino-4-methylpyridine)] (**1**), generated in situ, with $LnCl_3$ (Ln = Y, Sm) in THF affords $O(SiMe_2\text{-}Ap)_2YCl(THF)_2$ (**2**) or $O(SiMe_2\text{-}Ap)_2SmCl(THF)_3$ (**3**). In contrast, the reaction of one or two equivalents of dilithiated **1**, again generated in situ, with $LaBr_3$ in THF affords $O(SiMe_2\text{-}Ap)_2)_2LaLi(THF)_3$ (**4**). An X-ray structural analysis of **2** and **3** reveal the $O(SiMe_2\text{-}Ap)^{2-}$ ligand to bind in a planar tetradentate manner. Equivalent Sm–N distances in **3** indicate a delocalized binding mode. Compound **2** reacts with Bu_4NBH_4, $NaBH_4$ or $LiCH(SiMe_3)_2$ to give the corresponding "ate" complexes $O(SiMe_2\text{-}Ap)_2Y(BH_4)\text{-}Cl(THF)$ Bu_4N (**5**), $O(SiMe_2\text{-}Ap)_2Y(BH_4)_2Na(THF)_2$ (**6**) and $O(SiMe_2\text{-}Ap)_2Y(CH(TMS)_2)_2Li(THF)_3$ (**7**), respectively. The steric demand of the $O(SiMe_2\text{-}Ap)^{2-}$ ligand is not large enough to stabilize monoalkyl or monoborohydride complexes. Complex **4** has been used as an initiator for the ring-opening polymerization of ε-caprolactone or δ-valerolactone. In both cases an almost linear relation between the monomer-to-initiator ratio and the molecular weight of the obtained polyester is observed. By conducting the polymerization in neat ε-caprolactone at room temperature a solid polyester block is formed after 3 min (300000 $g \cdot mol^{-1}$, M_w/M_n 2.3).

Introduction

The most popular amido ligands in lanthanide chemistry are the silyl-substituted benzamidinates (Scheme 1, left).[1] Related to these ligands are deprotonated 2-aminopyridines (aminopyridinato ligands) when they are bound in a strained η^2 coordination mode (Scheme 1, right).



Scheme 1. Benzamidinate (left) and aminopyridinato (right) ligands

Only a few examples of such group 3 metal complexes (including lanthanides) have been described so far.[2] An advantage of aminopyridinato over amidinato ligands is the opportunity to connect two of them easily by a bridge between the amido nitrogen atoms,[3] thus giving additional possibilities in ligand and complex design. Furthermore, an increase in the stability of the metal-ligand bond (chelating effect) might be established, which would extend the active lifetime of such compounds when employed as catalysts. However, a disadvantage of the aminopyridinato ligands might be the lower steric demand of these ligands, since steric shielding is considered to be very important to prevent the formation of "ate" complexes. Recently, "ate" complexes have been shown to have very interesting applications in homogeneous catalysis[4][5] and coordination chemistry.[2][6] In this paper we report on the synthesis and structure of group 3 and lanthanide complexes that contain siloxane-bridged bisaminopyridinato ligands. Furthermore, the application of selected examples of such compounds in the ring-opening polymerization of lactones is described. Recently, the preparation of siloxane-bridged bisaminopyridinato complexes of the group 4 metals, including ethylene polymerization studies of these compounds, was reported.[7]

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Results and Discussion

Metal Complex Syntheses and Structures

1. Monochloro and Bis(bisaminopyridinato) Complexes

The reaction of one equivalent of dilithiated $O(SiMe_2\text{-}Ap\text{-}H)_2$ [Ap-H = -N(2-amino-4-methylpyridine)][7] (**1**), generated in situ, with $LnCl_3$ (Ln = Y, Sm) in THF affords **2** or **3** by a salt metathesis reaction (Scheme 2, above). Compounds **2** and **3** could be isolated from THF/ether solution after removal of the precipitated LiCl. They form crystals which are colorless (**2**) or light orange (**3**).

From the NMR spectroscopic data of **2** and **3** it can be inferred that the ligand array coordinates to the metal in a planar fashion. The ^1H and ^{13}C NMR spectra are consistent with C_{2v} monomeric structures in which the nuclei measured show a single set of signals. Single crystal X-ray diffraction analyses of **2** and **3** reveal each to have a monon-

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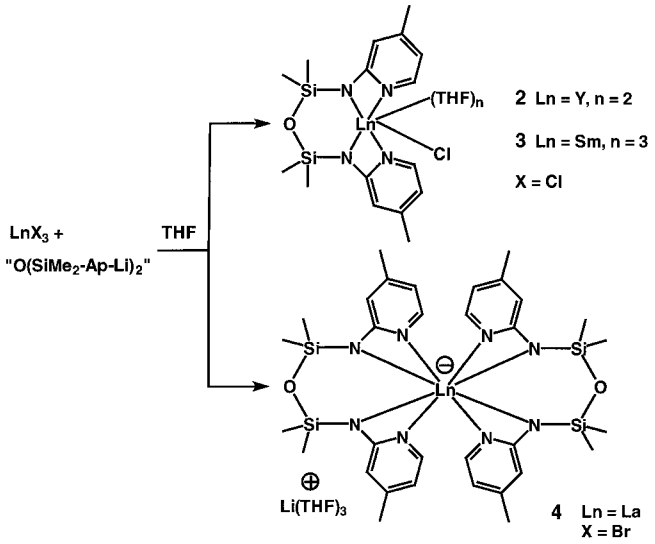


Scheme 2. Synthesis of monochloro and bis(bisaminopyridinato) lanthanoid complexes

uclear structure with the symmetry proposed from the NMR studies (see Figure 1 and 2, respectively).

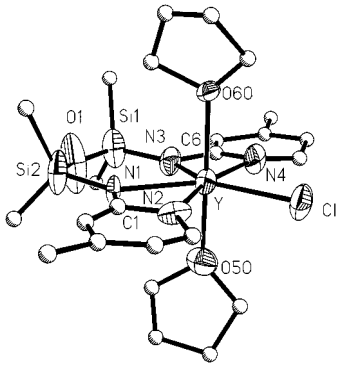


Figure 1. Structural representation of **2**; hydrogen atoms and disorders of the THF ligands are omitted for clarity; the thermal ellipsoids correspond to 30% probability; selected bond lengths [pm] and angles [deg]: Y−N1 246.5(14), Y−N2 249(2), Y−N3 227(2), Y−N4 236(2), Y−O50 221(2), Y−O60 240.9(13), Y−Cl 264.6(3), N1−C1 129(4), N2−C1 144(3), N3−C6 144(2), N4−C6 134(3); Si1−O1−Si2 148.2(9), N1−Y−N3 83.2(3), O50−Y−O60 178.6(4), O50−Y−Cl 89.1(5), O60−Y−Cl 92.1(4)

The X-ray analysis of **2** clearly shows that the ligand array coordinates to the metal in a planar fashion. The metal atom is surrounded by four nitrogen atoms within the equatorial plane of a pentagonal bipyramid. The apices of the pyramid are occupied by two molecules of solvent (THF), which appear to be rather loosely bound, since complex **2** readily loses coordinated THF. Experimental evidence for this was gained by a combined elemental analysis and ^{1}H NMR spectroscopic investigation. In contrast to the spectroscopic data showing two molecules of THF coordinating to the metal atom, the elemental analysis of a sample dried in vacuo indicates the presence of a single molecule of solvent. After drying at 150°C in vacuo for 15 min not a single THF ligand was found residing at the metal complex (by ^{1}H NMR spectroscopy). The presence of two coordinated THF ligands is shown by the X-ray analysis of **2** (Figure 1). Due to the larger ionic radius of Sm an increase in coordination number from Y to Sm is observed (Figure 2).

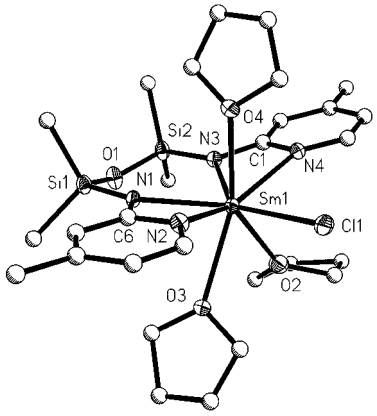


Figure 2. Structural representation of **3**; hydrogen atoms and disorder of one of the three THF ligands are omitted for clarity; the thermal ellipsoids correspond to 30% probability; selected bond lengths [pm] and angles [deg]: Sm1−N1 244.1(4), Sm1−N2 247.9(5), Sm1−N3 245.9(4), Sm1−N4 251.5(4), Sm1−O2 251.4(4), Sm1−O3 258.6(4), Sm1−O4 252.6(4), Sm1−Cl1 271.5(2), N1−C6 135.7(6), N2−C6 135.9(7), N3−C1 136.8(7), N4−C1 137.3(7); Si1−O1−Si2 141.2(3), N1−Sm1−N3 83.10(14), O2−Sm1−O3 65.45(14), O2−Sm1−Cl1 84.69(11), O3−Sm1−Cl1 92.83(10), O4−Sm1−Cl1 85.65(10)

The latter metal center has three additionally coordinated THF ligands. The equivalence of the samarium−nitrogen bond lengths indicates the existence of a delocalized binding mode, thus showing that the negative charge of the aminopyridinato moieties is not localized on the amido nitrogen atom. The reaction of one or two equivalents of dilithiated $O(SiMe_2\text{-}Ap\text{-}H)_2$, generated in situ, with $LaBr_3$ in THF affords **4** (see Scheme 2). The formation of **4** is independent of the ratio of **1** and $LaBr_3$ used as only the bis(bisaminopyridinato) complex was isolated. NMR spectroscopic data of **4** indicate a highly symmetric molecule, as only one set of signals is seen in the proton NMR spectrum.

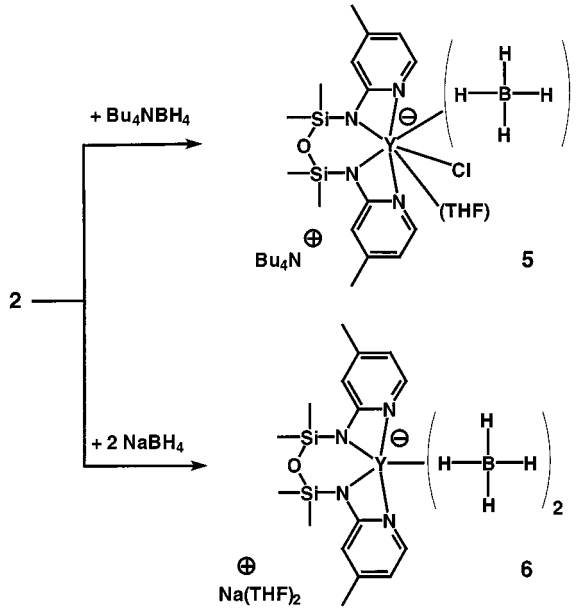
2. Yttrium Borohydride Complexes

The reactivity of **2** towards borohydride ions was examined by using either one equivalent of Bu_4NBH_4 (Scheme 3) or an excess of $NaBH_4$ in THF (Scheme 3). The reactions proceeded at room temperature within a few hours (see Experimental Section for details). The reaction of **2** with Bu_4NBH_4 gave **5**, while from the reaction with $NaBH_4$ complex **6** was isolated.

In contrast to sodium borohydride, which is insoluble in THF, compound **6** displays a high solubility in THF. Similarly, while **5** is very soluble in ether, Bu_4NBH_4 is nearly insoluble in this solvent. Compounds **5** and **6** were characterized by standard analytical methods. No resonances for the BH_4 groups could be seen in the ^{1}H NMR spectrum, probably due to the quadrupole moment of the boron nucleus. The IR signals in the range 2380−2130 cm^{-1} are characteristic of BH_4 vibrations.

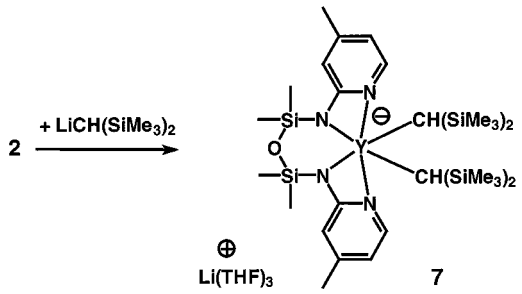
3. Alkyl Complexes

For the alkylation of **2** and **3**, a salt elimination route was chosen. As shown in Scheme 4, compound **2** was reacted



Scheme 3. Syntheses of yttrate complexes **5** and **6**

with an equimolar amount of $LiCH(SiMe_3)_2$ at low temperature. The reaction mixture was filtered to remove precipitated LiCl, concentrated in vacuo and cooled to promote crystallization, after which complex **7** was obtained as colorless needles at −40°C. Since **7** is prone to thermal decomposition it has to be stored at −30°C. The ^1H NMR spectrum of **7** contained a single signal set for the aromatic protons indicative of a symmetric molecule. The presence of three THF ligands can be concluded from the integration of the resonances in the NMR spectrum. The IR data is consistent with that of a coordinating bisaminopyridinato ligand and, together with the results of the elemental analysis, is in accordance with the proposed structure of **7** in Scheme 4.



Scheme 4. Synthesis of the yttrate complex **7**

The reaction of **3** with PhLi leads to biphenyl. The progress of this reaction at −40°C can easily be followed by the change of color of the reaction mixture from red to yellow and the precipitation of LiCl . On warming to 15°C the solution suddenly changed color . The clear, light yellow solution became dark brown, a color which is characteristic for Sm^{II} compounds. We tentatively ascribed this to a redox reaction in which samarium was reduced from Sm^{III} to Sm^{II} and the phenyl anion was oxidized. The reaction mixture was therefore examined for products of phenyl radicals, which one can assume were intermediates. By GC/MS, biphenyl was identified as a product of the reaction and this was confirmed by NMR spectroscopic studies. Recently, Fryzuk et al. have reported a similar reaction, which started with the attempted arylation of an yttrium(III) chloro complex by PhLi but yielded a biphenyl-dianion coordinated to two yttrium(III) complex fragments.[8] Since yttrium is not as easily reduced as samarium this reaction stops after phenyl coupling. The yttrium arene complex may be considered as a model for the intermediate in the reaction of **3** with PhLi.

Ring-Opening Polymerization of Lactones

The ring-opening polymerization of lactones is a useful method to produce biodegradable aliphatic polyesters.[9] Well-defined polymers of this sort have interesting applications, for instance, as surgical sutures and drug delivery systems.[10] Common polyesters are made from a condensation polymerization reaction starting from diols and dicarboxylic acids. A disadvantage of this method is that high temperatures and long reaction times are required to obtain high molecular weights. Furthermore, broad molecular weight distributions are observed. Lanthanocene complexes have been found to be initiators for the ring-opening polymerizations of ε-caprolactone and δ-valerolactone.[11] Recently, lanthanide "ate" complexes have been introduced as very efficient initiators.[5] However, the preferred linear relationship between the monomer to initiator ratio and the molecular weight was not observed, although molecular weights of up to 30000 $g \cdot mol^{-1}$ were obtained. Thus, the behavior of the aminopyridinato "ate" complex **4** as an initiator was investigated with regard to a linear relation between the monomer to initiator ratio and the molecular weight of the polyester, as well as the production of high molecular weights. Tables 1 and 2 show the results of these polymerization studies.

Table 1. Ring opening polymerization of ε-caprolactone with **4** as an initiator

$[M_0]/[I_0]$	M_n [$g \cdot mol^{-1}$]	M_w/M_n	Yield%
100	25000	1.7	61
200	40000	1.7	59
300	51000	1.7	70
400	54000	1.7	74

Table 2. Ring opening polymerization of δ-valerolactone with **4** as an initiator

$[M_0]/[I_0]$	M_n [$g \cdot mol^{-1}$]	M_w/M_n	Yield%
100	12000	1.7	39
200	15000	1.8	35
300	19000	2.0	48
400	27000	1.6	50

ε-Caprolactone and δ-valerolactone were used as monomers. In both cases an almost linear relation between the

monomer to initiator ratio and the molecular weight was observed. The high efficiency of the system is remarkable. By performing the polymerization in neat ε-caprolactone at room temperature a solid polyester block (300000 g·mol^{-1}, M_w/M_n 2.3) is formed after 3 min. Nevertheless, the thermodynamically stable γ-butyrolactone could not be polymerized with **4** as an initiator.

Conclusion

Several conclusions can be drawn from this study. Firstly, the monochloro complexes are readily accessible by salt metathesis reactions. Secondly, these metal complexes smoothly react with borohydrides and standard alkylating reagents to yield the corresponding "ate" complexes. The steric demand of the siloxane-bridged bisaminopyridnato ligands is not large enough to stabilize monoalkyl or monoborohydride complexes. Thirdly, bis(bisaminopyridinato) complexes are highly efficient initiators for the ring-opening polymerization of lactones.

Experimental Section

Materials and Procedures: Bis(trimethylsilyl)methyl lithium[12] and the bisaminopyridine O(SiMe$_2$-Ap-H)$_2$[7] were prepared according to literature procedures. All other reagents were obtained commercially and used as supplied. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in dried Schlenk-type glassware on a dual manifold Schlenk line interfaced to a high-vacuum line, or in an argon-filled glovebox (mBraun labmaster 130) with a high-capacity recirculator (<1.5 ppm O_2). Reaction solvents (Aldrich) and NMR solvents (Cambridge Isotope Laboratories all 99 atom% D) were freshly distilled from sodium tetraethylaluminate.

Physical Measurements: NMR spectra were recorded on a BRUKER ARX 400 instrument with a variable temperature unit. ^{1}H and ^{13}C chemical shifts are referenced to the solvent resonances and reported relative to TMS. ^{29}Si chemical shifts are reported relative to TMS. Melting points were determined in sealed capillaries on a BÜCHI 535 apparatus. Elemental analysis were performed with a Leco CHNS-932 elemental analyzer. X-ray diffraction data were collected on a STOE-IPDS diffractometer using graphite monochromated MoK_α radiation. The crystals were mounted in a cold nitrogen stream (**3**) or sealed inside a capillary (**2**). The structure was solved by direct methods (SHELXS-86)[13] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[14] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. See also Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-121918 (compound **2**) and CCDC-121919 (compound **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat. + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk]. Number-average molecular weights and molecular weight distributions of the isolated polymers were determined by gel permeation chromatography on a HP Liquid Chromatograph 1090 at 40°C using THF as the eluent and a universal calibration relative to polystyrene standards.

Table 3. Crystallographic details of the X-ray crystal structure analysis of **2** and **3**

compound	**2**	**3**
crystal system	monoclinic	monoclinic
space group	*Pn*	$P2_1/c$
a, Å	9.790(2)	14.524(3)
b, Å	14.585(3)	9.966(2)
c, Å	11.453(2)	23.759(5)
β, deg	104.15(1)	92.06(3)
V, Å^3	1585.7(5)	3436.8(12)
Z	2	4
crystal size, mm	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.4
ρ_{calcd}, g cm^{-3}	1.284	1.443
μ, cm^{-1} (MoK_α)	2.03	1.89
T, K	293	200
θ range, deg	2.30 < θ < 24.40	2.18 < θ < 24.28
no. of reflections	4689	9847
no. of reflections unique	2570	5476
no. of reflections obs. [$I > 2\sigma(I)$]	1247	3808
no. of parameters	273	359
ωR^2 (all data)	0.151	0.089
R value [$I > 2\sigma(I)$]	0.054	0.040

Syntheses of the Complexes 2−7. O(SiMe$_2$-Ap)$_2$YCl(THF)$_2$ (2): O(SiMe$_2$-Ap-H)$_2$ (3.11 g, 8.98 mmol) was dissolved in a mixture of 20 mL of hexane and 10 mL of THF and cooled to −78°C. While stirring, 17.96 mmol of *n*-butyllithium was added. This mixture was warmed to −40°C and stirred for 30 minutes to yield a colorless suspension. YCl_3 (1.76 g, 8.98 mmol) was added to 30 mL of THF and the mixture heated to reflux for 10 minutes. The resulting suspension was cooled to −40°C and at this temperature added to the suspension of the lithiated ligand. The reaction mixture was allowed to warm to ambient temperature and stirred for another 12 h; the solvent was then removed in vacuo. The residue was washed with 10 mL of hexane, filtered through a frit (G 4), and then washed with 20 mL of ether and filtered again. The combined filtrates were reduced in volume to 15 mL by vacuum evaporation, to give a colorless precipitate . Having stood for 12 h, the mixture was filtered and the filtrate cooled to −78°C. The crystalline product was obtained by filtration and dried in vacuo. Yield: 3.27 g (6.05 mmol, 67%), m.p. 233°C, (240°C dec.). − ^{1}H NMR (293 K, C_6D_6): δ = 7.69 (s, 2 H, broad, 6-H), 6.22 (s, 2 H, 3-H), 5.83 (broad, 2 H, 5-H), 3.65 (t, 8 H, *J* = 6.4 Hz, THF), 1.90 (s, 6 H, Me-pyridine), 1.12 (m, 8 H, THF), 0.59 (s, 12 H, Me−Si). − ^{13}C NMR (293 K, C_6D_6): δ = 170.6 (C-2), 150.1 (C-4), 145.2 (C-6), 112.4 (C-5), 110.3 (C-3), 69.8, 25.3 (THF), 21.6 (Me-pyridine), 1.9 (Me−Si). − ^{29}Si NMR (293 K, C_6D_6): δ = −15.5. − IR (nujol): $\tilde{\nu}$ = 1604 s, 1532 m (C=C), 1330 s, 1290 s, 1252 s (Me−Si), 1174 s, 1055, 1027, 999 vs (Si−O−Si), 891 s, 871 s (Me$_2$Si), 748 s, 583 s cm^{-1}. − $C_{24}H_{40}ClN_4O_3Si_2Y$ (613): calcd. C 47.01, H 6.58, N 9.14; found C 45.81, H 6.49, N 9.51. The lower value found for carbon is due to the loss of coordinated solvent (THF).

O(SiMe$_2$-Ap)$_2$SmCl(THF)$_3$ (3): To a solution of O(SiMe$_2$-Ap-H)$_2$ (2.92 g, 8.44 mmol) in 20 mL of THF was added 16.88 mmol *n*-butyllithium, dissolved in hexane, at −78°C. After stirring for 1 h at −78°C this solution was warmed to 20°C within another hour and then added to a suspension of $SmCl_3$ (3.25 g, 12.7 mmol) in 40 mL of THF. The reaction mixture was stirred for 12 h, and the solvent was then removed in vacuo to yield a viscous yellow oil which was redissolved in a mixture of 30 mL of ether and 10 mL of THF. A colorless microcrystalline solid precipitated. The supernatant solution was filtered and reduced in volume to 20 mL. Cooling to −30°C yielded light orange needles, which were collected

and dried in vacuo. The crystals easily lose coordinating solvent on vacuum drying. Yield: 1.27 g (2.11 mmol, 25%), mp: 82−86°C (solvent loss), 110−130°C, (230°C dec.). − ^{1}H NMR (293 K, [D$_8$]THF): δ = 10.76 (d, 2 H, *J* = 5.2 Hz, 6-H), 7.59 (s, 2 H, 3-H), 6.90 (d, 2 H, *J* = 5.2 Hz, 5-H), 3.61−3.55 (m, 8 H, THF), 2.70 (s, 6 H, Me-pyridine), 1.79−1.76 (m, 8 H, THF), 0.82 (s, 12 H, Me−Si). − ^{13}C NMR (293 K, [D$_8$]THF): δ = 186.1 (C-2), 150.4 (C-4), 148.3 (C-6), 115.6 (C-5), 110.0 (C-3), 68.3 (THF), 26.4 (THF), 22.4 (Me-pyridine), 2.4 (Me−Si). − ^{29}Si NMR (293 K, [D$_8$]THF): δ = −10.9. − IR (nujol): $\tilde{\nu}$ = 1605 s, 1532 m (C=C), 1324 m, 1288 m, 1249 s (Me−Si), 1174 s, 1056, 1025 vs (Si−O−Si), 888, 870 s, 785 vs (Me$_2$Si), 737 m, 583 m cm^{-1}. − $C_{20}H_{32}ClN_4O_2Si_2Sm$ (602): calcd. C 39.87, H 5.35, N 9.30; found C 39.63, H 5.24, N 9.13.

O(SiMe$_2$-Ap)$_2$)$_2$LaLi(THF)$_3$ (4): To a solution of O(SiMe$_2$-ApH)$_2$ (4.03 g, 11.5 mmol) in 50 mL of THF was added 23.4 mmol of BuLi at −78°C. After stirring for 30 min at this temperature the solution was allowed to warm to 20°C within 30 min. The solution was then added to a suspension of $LaBr_3$ (2.20 g, 5.82 mmol) in 50 mL of THF. The reaction mixture was stirred for 16 h at 20°C. After removal of precipitated LiBr by filtration the volume of solvent was reduced to 30 mL, and 20 mL of diethyl ether was added. Cooling the solution to −30°C yielded colorless crystals which were collected and dried in vacuo. Yield: 4.7 g (4.5 mmol, 77%), mp: 203−205°C. − ^{1}H NMR (293 K, [D$_8$]THF): δ = 7.55 (d, *J* = 4.9 Hz, 2 H, H-6), 5.69 (s, 2 H, H-3), 5.59 (d, *J* = 5.3 Hz, 2 H, H-5), 3.62 (m, 4 H, THF), 1.89 (s, 6 H, Me-pyridine), 1.77 (m, 4 H, THF), 0.11 (s, 6 H, Me−Si). − ^{13}C NMR (293 K, [D$_8$]THF): δ = 170.4 (C-2), 146.4 (C-4), 146.1 (C-6), 113.9 (C-5), 107.1 (C-3), 67.4 (THF), 26.3 (Me-pyridine), 25.2 (THF), 2.1 (Me−Si). − ^{29}Si NMR (293 K, [D$_8$]THF): δ = −19.8. − IR (nujol): $\tilde{\nu}$ = 1601 vs, 1530 s (arom.), 1377 s, 1331 m, 1294 s, 1245 s (Me−Si), 1178 s, 1026 s, 990 s (Si−O−Si), 881 s, 839 s, 792 vs (Me$_2$Si), 674 m, 574 s cm^{-1}. − $C_{44}H_{72}LaLiN_8O_5Si_4$ (1051): calcd. C 50.27, H 6.90, N 10.66; found C 49.81, H 7.06, N 10.82.

O(SiMe$_2$-Ap)$_2$Y(BH$_4$)Cl(THF) Bu$_4$N (5): Compound **2** (567 mg, 1.05 mmol) and tetrabutylammonium boranate (540 mg, 2.10 mmol) were dissolved in 10 mL of THF with stirring. The solution was reduced in volume to 2 mL, then 20 mL of ether was added and the solution was stirred for 1 h. After filtration a clear colorless solution with a characteristic blue fluorescence was obtained. The solvent was removed in vacuo within 2 h to furnish a highly viscous, sticky product. Yield: 330 mg, 0.414 mmol, 39%. − ^{1}H NMR (293 K, [D$_8$]THF): δ = 7.87 (d, *J* = 5.2 Hz, 2 H, 6-H), 5.86−5.84 (m, 4 H, 3-H, 5-H), 3.61 (m, 6 H, THF), 3.29 (m, 8 H, 1′-H), 2.01 (s, 6 H, Me-pyridine), 1.75−1.71 (m, 6 H, THF), 1.65−1.62 (m, 8 H, 2′-H), 1.38−1.32 (m, 8 H, 3′-H), 0.93 (t, *J* = 7.2 Hz, 12 H, 4′-H), 0.09 (s, 12 H, Me−Si). − ^{13}C{^{1}H} NMR: δ = 170.3 (C-2), 148.6 (C-4), 145.9 (C-6), 112.5 (C-5), 108.1 (C-3), 68.2 (THF), 59.1 (C-1′), 26.2 (THF), 21.5 (Me-pyridine), 20.4 (C-3′), 14.0 (C-4′), 1.5 (Me−Si). − ^{29}Si NMR: δ = −15.6. − IR (THF): $\tilde{\nu}$ = 2278 m, 2206 m, 2135 m (B-H), 1642 w, 1603 vs, 1563 m (aromat.) cm^{-1}. − $C_{36}H_{72}BClN_5O_2Si_2Y$ (797): C 54.16, H 9.09, N 8.77, Cl 4.44; found C 54.26, H 10.21, N 8.82, Cl 4.55.

O(SiMe$_2$-Ap)$_2$Y(BH$_4$)$_2$Na(THF)$_2$ (6): With stirring NaBH$_4$ (107 mg, 2.81 mmol) was added to a solution of **2** (759 mg, 1.40 mmol) in 10 mL of THF. The resulting mixture was stirred for 72 h at 20°C and then filtered. The colorless filtrate was reduced in volume to 5 mL by vacuum evaporation. Cooling to −30°C afforded colorless needles. Yield: 292 mg, 0.523 mmol, 37%, mp: 164°C: subl. − ^{1}H NMR (293 K, C_6D_6): δ = 8.42 (broad, 2 H, 6-H), 6.17 (s, 2 H, 3-H), 6.03 (d, *J* = 5.0 Hz, 2 H, 5-H), 3.74 (t, *J* = 6.5 Hz, 8 H, THF), 1.86 (s, 6 H, Me-pyridine), 1.10 (m, 8 H, THF), 0.46 (s, 12 H, Me−Si). − ^{13}C NMR (293 K, C_6D_6): δ = 170.9 (C-2), 150.6 (C-4), 146.1 (C-6), 112.7 (C-5), 110.2 (C-3), 70.7 (THF), 25.2 (THF), 21.5 (Me-pyridine), 1.8 (Me−Si). − ^{29}Si NMR (293 K, C_6D_6): δ = −15.6. − IR (nujol): $\tilde{\nu}$ = 3316 w, 2374, 2297, 2223 m (BH$_4$), 1605 vs, 1566 w, 1532 m (C=C), 1377 m, 1329 s, 1290, 1252 s (Me−Si), 1175 s, 1057, 1028 vs (Si−O−Si), 999 m, 970 m, 892, 872 s (Me$_2$Si), 785, 776 s, 585 m cm^{-1}. − $C_{20}H_{40}B_2N_4NaO_2Si_2Y$ (558): calcd. C 43.03, H 7.22, N 10.04, Cl 0.00; found C 43.88, H 7.55, N 9.15, Cl 0.16.

O(SiMe$_2$-Ap)$_2$Y(CH(TMS)$_2$)$_2$Li(THF)$_3$ (7): An ethereal solution of bis(trimethylsilyl)methyllithium (0.973 mmol) was added dropwise to a solution of **2** (526 mg, 0.973 mmol) in 10 mL of ether. A colorless solid precipitated. After standing for 16 h at 4°C the supernatant solution was filtered through a frit (G 4). The filtrate was evaporated to dryness and the residue redissolved in a mixture of 20 mL of pentane and 3 mL of ether and filtered again. Cooling the filtrate to −78°C afforded a yellowish crystalline product. Yield: 224 mg, 0.367 mmol, 38%, mp: 175°C subl. (dec.). − ^{1}H NMR (293 K, C_6D_6: δ = 7.67 (s, broad, 2 H, 6-H), 6.22 (s, 2 H, 3-H), 6.02 (d, *J* = 4.8 Hz, 2 H, 5-H), 3.42 (broad, 12 H, THF), 1.84 (s, 6 H, Me-pyridine), 1.20 (s, 12 H, THF), 0.51 (s, 12 H, Me−Si−O), 0.40−0.35 (m, 36 H, Me−Si−C), −0.36 (s, 1 H, HC-Y), −0.82 (s, 1 H, HC−Y). − ^{13}C NMR (293 K, C_6D_6): δ = 169.6 (C-2), 150.7 (C-4), 144.2 (C-6), 113.8 (C-5), 110.9 (C-3), 69.2 (THF), 65.8 (ether), 25.2 (THF), 21.5 (Me-pyridine), 15.3 (ether), 6.6 (Me−Si), 4.4 (Me−Si), 1.7 (Me−Si), 1.5 (Me−Si). − ^{29}Si NMR (293 K, C_6D_6: δ = −0.12 (Me$_2$Si), −7.9 (Me$_3$Si), −9.1 (Me$_3$Si). − IR (nujol): $\tilde{\nu}$ = 1606 vs, 1533 w (C=C), 1377 m, 1329 m, 1296 m, 1247 s (Me−Si), 1178 m, 1045 vs, 1027 vs (Si−O−Si), 994 m, 968 w, 892 s, 862, 844, 826, 781 vs (Me$_2$Si), 676 m, 656 m, 588 m, 428 m cm^{-1}. − $C_{42}H_{86}LiN_4O_4Si_6Y$ (1114): calcd. C 51.71, H 8.89, N 5.74; found: C 51.36, H 8.30, N 5.94.

Polymerization: In a typical run ε-caprolactone/δ-valerolactone was added by syringe to a solution of **4** (24 μmol) in 10 mL THF at 20°C with vigorous magnetic stirring. After 30 min the polymerization was quenched by addition of 200 mL methanol. The precipitated polymer was redissolved in THF and precipitated again from methanol (250 mL). The polymer was filtered and dried in vacuo.

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