Di- and Trivalent Lanthanide Complexes Stabilized by Sterically Demanding Aminopyridinato Ligands

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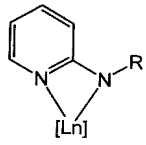
Deprotonation of Ap*H {Ap*H = (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine} and Ap′H {Ap′H = (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine} using KH leads to polymeric $[Ap^*K]_n$ and $[Ap'K]_n$ which undergo clean salt metathesis reactions with $NdCl_3$ in THF forming $[Nd(Ap^*)Cl_2(THF)_2]_2$ and $[Nd(Ap')_2Cl(THF)]$, respectively. Ethylene polymerization activities of the two chloro complexes (after activation with MAO) were studied. Derivatization of the chloro compounds proceeds without ate complex formation, for instance the reaction of $[Nd(Ap')_2Cl(THF)]$ with one equiv. of $[K\{N(SiMe_3)_2\}]$ leads to the "THF-free" silylamide $[Nd(Ap')_2\{N(SiMe_3)_2\}]$. Furthermore rare examples of heteroleptic amido-iodo complexes of selected divalent lanthanides can be stabilized by deprotonated Ap*H. Reaction of $[Ap^*K]_n$ with $[LnI_2(THF)_3]$ (Ln = Yb, Sm) in THF leads, after workup in hexane, to $[Yb(Ap^*)I(THF)_2]_2$ and $[Sm(Ap^*)I(THF)_2]_2$. All lanthanide complexes, four of them are paramagnetic, were characterized by X-ray crystal structure analysis. These compounds exhibit an excellent solubility in nonpolar solvents like hexane.

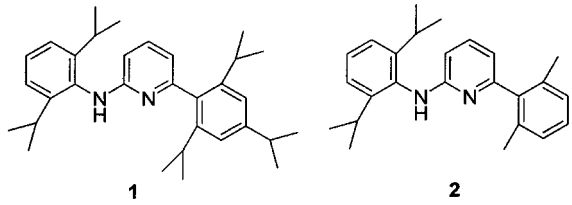
Introduction

During the renaissance[1] of amido[2] metal chemistry, aminopyridinato ligands (Ap)[3] have been used extensively to stabilize lanthanide (Ln) complexes. These compounds (Scheme 1) have been shown to exhibit unusual stoichiometric and catalytic reactivity.[4]



Scheme 1. An aminopyridinato ligand in its strained η^2 binding mode, typical for early transition metals and lanthanides ([Ln] = lanthanide moiety; R = aryl, silyl or alkyl substituent).

The size of the aminopyridinato ligands used thus far has been relatively small, resulting in a low steric demand of the metal, especially in the plane perpendicular to the pyridine moiety. This, in turn, gives rise to highly nitrogen-coordinated lanthanide complexes. Recently, we described the preparation of bulky aminopyridinato ligands by the introduction of 2,6-alkylphenyl substituents at the amido-N atom and also in the 6-position of the pyridine ring (Scheme 2).[5] Here, we report on synthesis, structure and reactivity of lanthanide complexes stabilized by deprotonated **1** and **2**.



Scheme 2. Proligands Ap*H (**1**) and Ap′H (**2**).

The maximum atom-to-atom distance in deprotonated **1** (determined from its Li salt[5] is 15 Å (vector **a** in Scheme 3, top). Approximately perpendicular to it is vector ***b*** = 8 Å. Comparing these measurements with those of the bulky, η^5-coordinated Cp*-ligand[6] (Cp* = pentamethylcyclopentadienyl) (Scheme 3, bottom), which has a distance of **a** = ***b*** = 6.2 Å, indicates that deprotonated **1** would be effective for the protection of large metal ions such as lanthanides. Furthermore, the stabilization of mono-amide [mono-(aminopyridinato)] complexes, in which ligand redistribution is blocked, should become possible.

The size of deprotonated **2** is somewhat smaller than deprotonated **1** with ***a*** = 13 Å and ***b*** = 8 Å.

Results and Discussion

Synthesis and Structure of Neodymium Complexes

The reactions of the lithium salts of **1** or **2** (prepared by deprotonation in situ with BuLi) with $NdCl_3$ did not result

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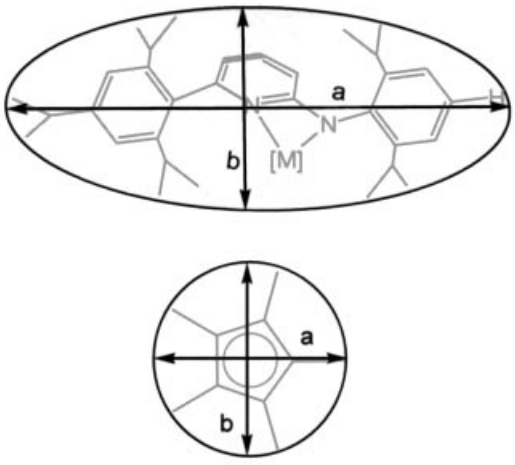
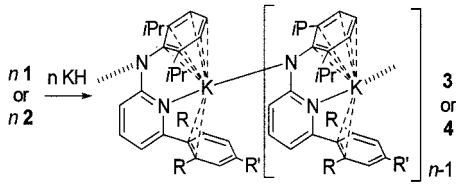


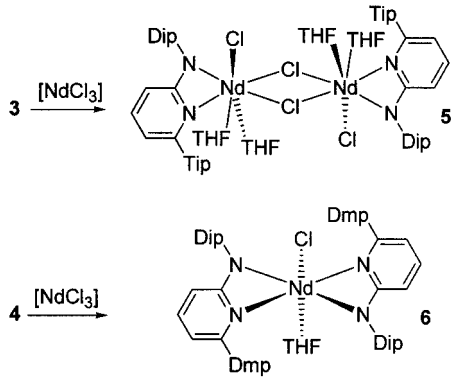
Scheme 3. Description of the steric demand of deprotonated **1** in comparison to Cp*.

in the isolation of a neodymium complex (only starting material was recovered). Deprotonation of **1** or **2** using KH gives rise to polymeric products **3** and **4**, as shown in Scheme 4.[5]



Scheme 4. Synthesis of **3** (R, R′, *i*Pr = isopropyl) and **4** (R = methyl, R′ = H).

Compounds **3** and **4** react with [$NdCl_3$] in a salt metathesis reaction affording **5** and **6**, see Scheme 5. No ate complex formation was observed. Compounds **5** and **6** were characterized by X-ray crystal structure analysis. Experimental details are summarized in Table 1. The molecular structure of **5** is shown in Figure 1.



Scheme 5. Synthesis of **5** and **6** (Dip = 2,6-diisopropylphenyl, Tip = 2,4,6-triisopropylphenyl, Dmp = 2,6-dimethylphenyl).

These investigations revealed **5** to be a dinuclear mono(aminopyridinato) complex. Reacting K to Nd ratios of 1:1 or 2:1 gave rise to the same product. The steric bulk of deprotonated **1** seems to favor the formation of a one to one Ap to Ln ratio. The N–Nd–N angle (53°) underlines the strained nature of the aminopyridinato coordination and the different Nd–N distances indicate a localization of the anionic function of the ligand at the amido-N atom – a classic amido−metal bond and a standard pyridine–neodymium bond. The amido-*N*···neodymium distance (2.380 Å) is in accordance with the reported values from the literature (standard value 2.356 Å[7]), as is the pyridine-N···neodymium distance at 2.659 Å (standard value 2.670 Å[8]). This is in contrast to the coordination of silylaminopyridinato lanthanide complexes, where a delocalized binding mode, including equivalent metal···nitrogen distances, has been observered in all compounds described so far.[4] The molecular structure of **6** is shown in Figure 2.

Table 1. Details of the X-ray crystal structure analyses of **5**, **6**, **7**, **8**, and **9**.

Compound	**5**	**6**	**7**	**8**	**9**
Crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	10.266(2)	12.985(3)	12.4893(4)	10.972(5)	12.059(5)
b [Å]	12.340(3)	14.336(3)	26.6564(7)	13.144(5)	17.584(5)
c [Å]	18.481(4)	14.377(3)	18.9051(6)	18.497(5)	19.978(5)
α [°]	84.31(3)	104.45(3)		84.183(5)	
β [°]	76.41(3)	91.17(3)	97.121(3)	78.661(5)	97.907(5)
γ [°]	71.98(3)	99.73(3)		82.795(5)	
V [Å^3]	2163	2549	6245	2587	4196
Z	1	2	4	1	2
Crystal size [mm^3]	0.36×0.31×0.15	0.21×0.18×0.16	0.29×0.22×0.20	0.45×0.31×0.28	0.11×0.06×0.05
$\rho_{calcd.}$ [g cm^{-3}]	1.251	1.260	1.176	1.340	1.389
μ [mm^{-1}]	1.355	1.110	0.909	2.443	2.167
T [K]	293	173	193	193	193
$\theta_{max.}$ [°]	26.06	25.99	26.05	25.95	26.34
No. of reflections unique	7737	9350	12305	10074	8264
No. of reflections obsd. [$I > 2\sigma(I)$]	6238	3982	8494	8504	2636
No. of parameters	426	562	631	455	195
wR_2 (all data)	0.142	0.127	0.073	0.131	0.366
R value [$I > 2\sigma(I)$]	0.057	0.056	0.030	0.042	0.131

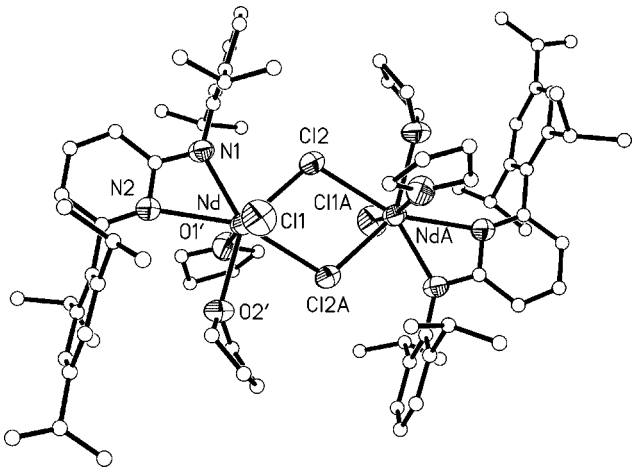


Figure 1. Molecular structure of **5** (ellipsoids correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: Nd−N1 2.380(4), Nd−O2′ 2.510(4), Nd−O1′ 2.510(4), Nd−Cl1 2.6443(19), Nd−N2 2.659(4), Nd−Cl2 2.7919(17), Nd−Cl2A 2.8511(17); Nd−Cl2−NdA 108.37(5), Cl1−Nd−Cl2 99.81(6), N1−Nd−N2 53.25(14).

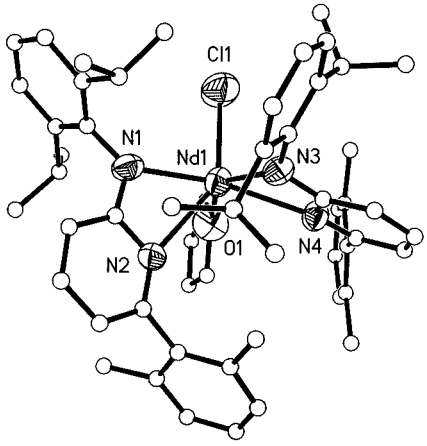
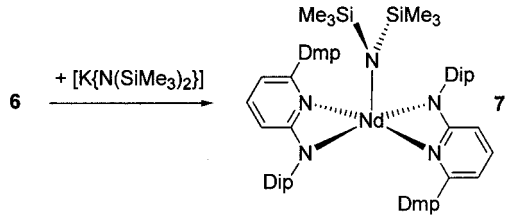


Figure 2. Molecular structure of **6** (ellipsoids correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: Nd1−N1 2.361(6), Nd1−N3 2.386(7), Nd1−O1 2.442(7), Nd1−N4 2.569(6), Nd1−Cl1 2.599(3), Nd1−N2 2.622(6), Nd1−C1 2.936(8); N3−Nd1−N4 54.9(2), N1−Nd1−Cl1 90.50(17), N3−Nd1−Cl1 103.37(16), N4−Nd1−Cl1 107.91(15), N1−Nd1−N2 54.1(2), Cl1−Nd1−N2 142.91(14).

In contrast to **5** a bis(aminopyridinato) complex is formed which is monomeric in the solid state. Despite the fact that the differences of the steric bulk of deprotonated **1** and **2** are rather small in comparison to the size of the ligands, selective formation of mono- or bis(aminopyridinato) complexes are observed. The neodymium···N distances of **6** are indicative of a localization of the anionic function. This appears to be a general phenomenon and is illustrated by the 90° dihedral angle between the pyridine plane and arylamido plane. It is probable that the two alkyl substituents prevent an interaction between the two π-systems. In silylaminopyridinato lanthanide complexes the pyridine π-system may interact with the silicon atom to cause further delocalization. This delocalization may go some way to explain the parity of two N–Ln bonds in silylaminopyridinato ligands. Compound **5** and **6** are soluble in nonpolar solvents such as hexane and salt metathesis reactions proceed in this solvent without ate complex formation. The reaction of **6** with one equiv. of [K{N(SiMe$_3$)$_2$}] leads to the silylamide **7**, uncoordinated by THF (Scheme 6).



Scheme 6. Synthesis of **7**.

Compound **7** was characterized by X-ray crystal structure analysis. Experimental details are summarized in Table 1. The molecular structure of **7** is shown in Figure 3.

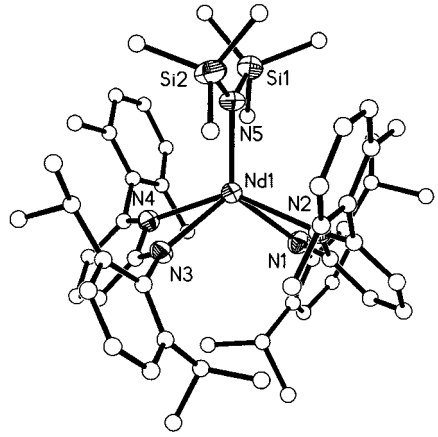
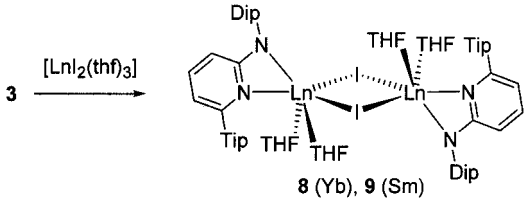


Figure 3. Molecular structure of **7** (ellipsoids correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: Nd1−N5 2.280(2), Nd1−N3 2.407(2), Nd1−N1 2.414(2), Nd1−N2 2.544(2), Nd1−N4 2.552(2); N5−Nd1−N3 123.78(8), N5−Nd1−N1 125.18(8), N5−Nd1−N2 108.02(8), N1−Nd1−N2 54.56(7), N5−Nd1−N4 110.50(8), N3−Nd1−N4 54.57(7).

The coordination can be described as rectangular pyramidal with the four aminopyridinato-N atoms forming the rectangle. As far as we are aware the silylamido–Nd bond length represents the shortest observed so far and should indicate a highly Lewis-acidic metal center. Compounds **5** and **6** were tested as catalysts for ethylene polymerization after activation with MAO. The complexes were dissolved in toluene and treated with MAO (aluminium to catalyst ratio = 250:1). A 1-L laboratory autoclave was charged with the catalyst solution and an ethylene overpressure of 10 bar was applied at 60 °C for 30 minutes. Compounds **5** and **6** showed activities of 51.4 and 42.4 $kg_{polyethylene}\,mol_{cat}^{-1}\,h^{-1}\,bar^{-1}$, respectively. These moderate activities[9] indicate the potential of these compounds in olefin polymerization. Detailed studies of olefin insertion into neutral or cationic lanthanide complexes are underway.

Synthesis and Structure of the Heteroleptic Ytterbium and Samarium Complexes

Pioneering work by Evans and coworkers[10,11] has shown that divalent lanthanide complexes exhibit a particularly rich reaction chemistry owing to the accessibility of different oxidation states;[12] for example, although $[Cp^*_2Sm]$ and $[Cp^*_2Sm(THF)_2]$ do not possess a metal–carbon bond they both show polymerization activity towards ethylene[13,14] The majority of this chemistry has been carried out utilizing homoleptic Cp* complexes. However, complexes incorporating a single Cp* ligand and a second anionic ligand (heteroleptic compounds), which may allow for further tuning of the reactivity, have received inadequate attention. This is partially due to the low stability of the mono-ligated starting materials. For example, the compounds $[(Cp^*)Sm(\mu\text{-}I)(THF)_2]_2$ [15] and $[(Me_3Si)_2NSm(\mu\text{-}I)(DME)(THF)]_2$ [16] (DME = dimethoxyethane) have been described and are reported to undergo facile ligand redistribution to give $[SmI_2(THF)_x]$ and $[SmL_2]$ [L = Cp*, $(Me_3Si)_2N$]. Divalent "heteroleptics" have been well documented in the case of donor-functionalized Cp-ligands but rarely described for alkoxy and amido ligands.[16,17] We expected deprotonated **1** to be an excellent candidate for the stabilization of such divalent complexes. The reaction of **3** with $[LnI_2(THF)_3]$ (Ln = Yb, Sm) in THF leads, after workup in hexane, to mono-iodido complexes, which prove to be binuclear in the solid state (Scheme 7). Experimental details of the X-ray crystal structure analyses are summarized in Table 1.



Scheme 7. Synthesis of **8** and **9**.

The molecular structures of **8** and **9** are shown in Figure 4 and Figure 5, respectively. The coordination of the two Yb centers of **8** is best described as octahedral with a dihedral angle of 95.1° between the Yb1–Yb1A–I1–I1A plane and the pyridine planes. Proton NMR spectra of **8** ([D_8]THF, [D_8]toluene) show a single signal set with well-resolved signals for the isopropyl groups in $C_6D_5CD_3$.

Since the paramagnetic nature of **9** prevents structural characterization by NMR spectroscopy, X-ray analysis was performed. Only very weak diffracting crystals of **9** could be obtained. However, the connectivity could be established. Owing to the low quality of structural data, a detailed discussion of bond length and angles is waived. The molecular structure of **9** is similar to that of **8** but the structures are not isomorphous.

Conclusions

Deprotonated **1** is an excellent ligand for the stabilization of mono(aminopyridinato) complexes of di- and trivalent lanthanides. The steric demands of this ligand result in a reduction of ligand redistribution during synthesis. Structurally, its lanthanide complexes can be compared to that of other bulky amide-containing compounds, such as troponiminate or amidate complexes but the chemistry should be somewhat different owing to higher ligand asymmetry. Surprisingly, deprotonated **2** gives selectively a bis(aminopyridinato) complex for neodymium, despite the relatively small difference in the structural size when compared with **1**. This study underlines the importance of fine-tuning, even surely in the "nano range".

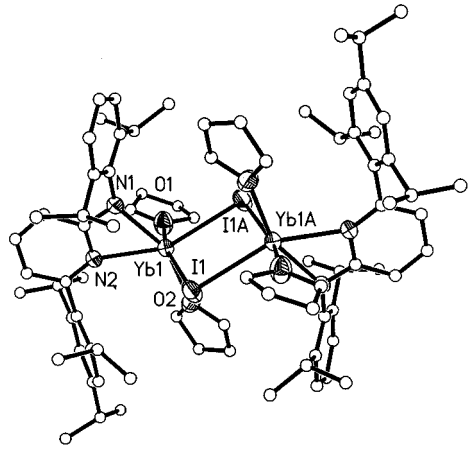


Figure 4. Molecular structure of **8** (ellipsoids correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: Yb1−N1 2.423(4), Yb1−O2 2.432(4), Yb1−O1 2.445(4), Yb1−N2 2.508(4), Yb1−C1 2.922(5), Yb1−I1 3.1225(10), Yb1−I1 3.1241(8), I1−Yb1 3.1225(10); N1−Yb1−O2 156.82(14), N1−Yb1−O1 97.23(15), O2−Yb1−O1 81.22(15), N1−Yb1−N2 55.30(13), O2−Yb1−N2 101.54(13), O1−Yb1−N2 87.55(14), N1−Yb1−I1A 104.44(10), O2−Yb1−I1A 98.42(10), O1−Yb1−I1A 83.99(11), N2−Yb1−I1A 156.84(9), N1−Yb1−I1 97.46(10), O2−Yb1−I1 87.29(10), O1−Yb1−I1 164.43(10), N2−Yb1−I1 105.12(9), C1−Yb1−I1 102.77(9), I1−Yb1−I1A 87.36(3).

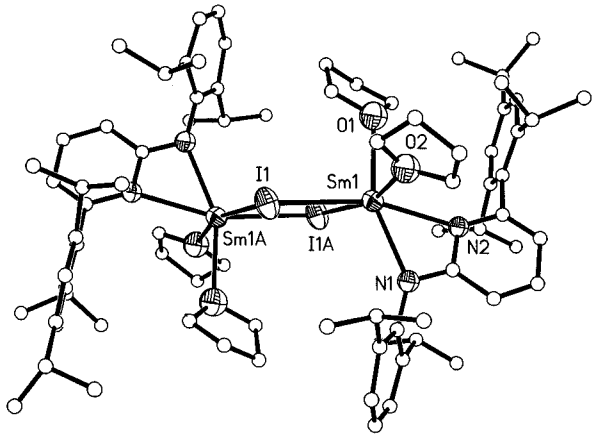
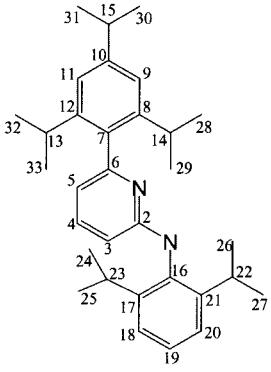


Figure 5. Molecular structure of **9** (ellipsoids correspond to the 50% probability level).

Experimental Section

General Procedures: All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried (CaH_2) and distilled prior to use. NMR spectra were obtained using either a Bruker ARX 250, Bruker DRX 500, Varian Unity Inova 400 or 300 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out with an Elementar Vario EL III. **1**, **2**, **3**, and **4**[5] as well as [$LnI_2(THF)_3$] (Ln = Yb, Sm)[18] were synthesized following literature procedures. Other starting materials were purchased from commercial suppliers. X-ray crystal structure analyses were performed with a STOE-IPDS I or II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[19] SHELXL97,[20] and WinGX.[21] CCDC-251807 (for **5**), -251808 (for **6**), -251809 (for **7**), -251810 (for **8**), and CCDC-251811 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of the Lanthanide Complexes



[Nd(Ap*)Cl_2(THF)$_2$]$_2$ (5): [$NdCl_3$] (0.38 g, 1.50 mmol), **3** (0.75 g, 1.50 mmol) and THF (40 cm^3) were added to a flask, and the mixture was stirred for 15 h. The solvent was removed under vacuum and hexane was added (30 cm^3). The light blue reaction mixture was filtered and on standing at room temperature for 2 h pale blue crystals of the title complex formed (0.80 g, 48%). $C_{80}H_{118}Cl_4N_4Nd_2O_4$ (1630): calcd. C 58.94, H 7.30, N 3.44; found C 58.95, H 7.14, N 3.05. Highly resolved NMR spectroscopic data could not be obtained. (2:1 Ligand/Nd reaction resulted in the formation of **5**.)

[Nd(Ap′)$_2$Cl(THF)] (6): [$NdCl_3$] (0.34 g, 0.93 mmol), **4** (0.74 g, 1.87 mmol) and THF (40 cm^3) were added to a flask, and the mixture was stirred for 24 h. The solvent was removed under vacuum and hexane was added (30 cm^3). The light blue reaction mixture was filtered and the filtrate allowed to stand at room temperature for 2 h whereupon small green-blue crystals of the title complex formed (0.37 g, 64%). $C_{54}H_{66}ClN_4NdO$ (967): calcd. C 67.08, H 6.88, N 5.79; found C 66.85 H 7.17, N 5.61. Highly resolved NMR spectroscopic data could not be obtained.

[Nd(Ap′)$_2${N(SiMe$_3$)$_2$}]•(hexane) (7): Hexane (30 cm^3) was added to **6** (0.11 g, 0.11 mmol) and [K{N(SiMe$_3$)$_2$}] (0.02 g, 0.11 mmol) and the mixture was stirred for 15 h. The reaction mixture was filtered and the filtrate concentrated to ca. 15 cm^3. The reaction mixture was cooled to –20 °C and on standing for 12 h pale blue crystals of the title complex were afforded (0.06 g, 42%). $C_{68}H_{104}N_5NdSi_2$ (1192): calcd. C 68.52, H 8.79, N 5.88; found C 68.85, H 7.98, N 6.31. Highly resolved NMR spectroscopic data could not be obtained.

[Yb(Ap*)I(THF)$_2$]$_2$ (8): [$YbI_2(THF)_3$] (0.70 g, 1.09 mmol), **3** (0.54 g, 1.09 mmol) and THF (40 cm^3) were added to a flask, and the mixture was stirred for 15 h. The solvent was removed under vacuum and a mixture of toluene (20 cm^3)/hexane (10 cm^3) was added. The red suspension was filtered and upon standing at –20 °C for 48 h, dark red crystals (suitable for X-ray analysis) of the title complex formed (0.80 g, 82%). $C_{80}H_{118}I_2N_4O_4Yb_2$ (1798): calcd. C 53.39, H 6.61, N, 3.11; found C 52.85, H 6.38, N 2.96. ^{1}H NMR (400 MHz, C_7D_8, 298 K): δ = 1.22 (d, ^3J = 7.0 Hz, 12 H, $H^{28,29,32,33}$), 1.27 (d, ^3J = 7.0 Hz, 6 H, $H^{24,25,26,27}$), 1.34 (d, ^3J = 7.0 Hz, 6 H, $H^{30,31}$), 1.35 (br, 8 H, β-CH_2, THF), 1.48 (d, ^3J = 7.0 Hz, 6 H, $H^{24,25,26,27}$), 2.78 (sept, ^3J = 7.0 Hz, 1 H, H^{15}), 3.28 (sept, ^3J = 7.0 Hz, 2 H, $H^{13,14}$), 3.41 (br, 8 H, α-CH_2, THF), 3.85 (sept, ^3J = 7.0 Hz, 2 H, $H^{22,23}$), 5.65 (d, ^3J = 8.4 Hz, 1 H, H^3), 5.85 (d, ^3J = 6.8 Hz, 1 H, H^5), 6.76 (dd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, 1 H, H^4), 7.04 (s, 2 H, $H^{9,11}$), 7.11 (vt, ^3J = 8.0 Hz, 1 H, H^{19}), 7.23 (d, ^3J = 8.0 Hz, 2 H, $H^{18,20}$) ppm. ^{13}C NMR (100.5 MHz, C_7D_8, 298 K): δ = 25.3 (s, $C^{30,31}$), 25.7 (s, $C^{24,25,26,27}$), 26.3 (s, β-CH_2, THF), 26.5 (s, $C^{28,29,32,33}$), 26.6 (s, $C^{24,25,26,27}$), 26.7 (s, $C^{28,29,32,33}$), 28.9 (s, $C^{22,23}$), 31.3 (s, $C^{13,14}$), 35.7 (s, C^{15}), 70.1 (s, α-CH_2, THF), 108.5 (s, C^3), 109.0 (s, C^5), 121.7 (s, $C^{9,11}$), 123.5 (s, C^{19}), 124.7 (s, $C^{18,20}$), 138.3 (s, C^4), 139.3 (s, C^7), 144.8 (s, $C^{17,21}$), 147.9 (s, C^{10}), 149.26 (s, $C^{8,12}$), 149.32 (s, C^{16}), 156.9 (s, C^6), 171.0 (s, C^2) ppm.

[Sm(Ap*)I(THF)$_2$]$_2$ (9): THF (40 cm^3) was added to the solids [$SmI_2(THF)_3$] (0.62 g, 1.00 mmol) and **3** (0.99 g, 1.00 mmol) and the mixture was stirred for 15 h. The solvent was removed in vacuo and hexane (10 cm^3) was added. The dark blue suspension was filtered and on standing at –20 °C for 72 h small dark blue crystals (suitable for X-ray analysis) of the title complex formed (0.23 g, 26%). $C_{80}H_{118}I_2N_4O_4Sm_2$ (1754): calcd. C 54.77, H 6.78, N 3.19; found C 53.72, H 6.67, N 3.30. Highly resolved NMR spectroscopic data could not be obtained.

Polymerization of Ethylene: The complex (≈ 20 mg) was dissolved in 15 cm^3 of toluene and treated with MAO solution (30% in toluene; aluminium to catalyst ratio = 250:1). The catalyst mixture was transferred to a larger flask and *n*-pentane (250 cm^3) was added. A BÜCHI laboratory autoclave (1 L) was charged with the catalyst solution and an ethylene overpressure of 10 bar was applied at 60 °C for 30 minutes. The reaction was stopped by relieving the pressure in the reactor. The polymers were washed with hydrochloric acid and acetone and then air-dried.

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[1] R. Kempe, *Angew. Chem.* **2000**, *112*, 478–504; *Angew. Chem. Int. Ed.* **2000**, *39*, 468–493.
[2] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Norwood Ltd., Chichester, **1980**.

[3] For a microreview on aminopyridinato ligands please see: R. Kempe, *Eur. J. Inorg. Chem.* **2003**, 791–803.
[4] For a review summarising lanthanide chemistry please see: R. Kempe, H. Noss, T. Irrgang, *J. Organomet. Chem.* **2002**, 647, 12–20.
[5] N. M. Scott, T. Schareina, O. Tok, R. Kempe, *Eur. J. Inorg. Chem.* **2004**, 3297–3304.
[6] R. Beckhaus, J. Oster, R. Kempe, A. Spannenberg, *Angew. Chem.* **1996**, *108*, 1636–1638; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1565–1567.
[7] Evaluation of all Nd−silylamido bond lengths stored in the Cambridge Crystallographic Data Base (November **2003**); number: 21, mean: 2.356, max.: 2.406, min.: 2.323.
[8] Evaluation of all Nd−pyridine (non-connected) bond lengths stored in the Cambridge Crystallographic Data Base (November **2003**); number: 10, mean: 2.670, max.: 2.741, min.: 2.555.
[9] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447.
[10] W. J. Evans, *Polyhedron* **1987**, *6*, 803–835.
[11] W. J. Evans, *Coord. Chem. Rev.* **2000**, *206*, 263–283.
[12] L. R. Morss, *Chem. Rev.* **1976**, *76*, 827–841.
[13] W. J. Evans, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1990**, *112*, 2314–2324.
[14] W. J. Evans, D. M. DeCoster, J. Greaves, *Macromolecules* **1995**, *28*, 7929–7936.
[15] W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 941–946.
[16] W. J. Evans, D. K. Drummond, H. M. Zhang, J. L. Atwood, *Inorg. Chem.* **1988**, *27*, 575–579.
[17] a) L. Hasinoff, J. Takats, X. W. Zhang, A. H. Bond, R. D. Rogers, *J. Am. Chem. Soc.* **1994**, *116*, 8833–8834; b) G. H. Maunder, A. Sella, D. A. Tocher, A. Derek, *J. Chem. Soc., Chem. Comm.* **1994**, *23*, 2689–2690; c) G. R. Giesbrecht, C. Chunming, A. Shafir, J. A. R. Schmidt, J. Arnold, *Organometallics* **2002**, *21*, 3841–3844; d) E. A. Fedorova, N. V. Glushkova, M. N. Bochkarev, H. Schumann, H. Hemling, *Izv. Akad. Nauk, SSSR Ser. Khim. (Russ) (Russ. Chem. Bull.)* **1996**, *8*, 2101–2104; e) I. L. Fedushkin, S. Dechert, H. Schumann, *Organometallics* **2000**, *19*, 4066–4076;; f) D. J. Duncalf, P. B. Hitchcock, G. A. Lawless, *Chem. Commun.* **1996**, *2*, 269–271; g) A. A. Trifonov, E. N. Kirillov, S. Dechert, H. Schumann, M. N. Bochkarev, *Eur. J. Inorg. Chem.* **2001**, *12*, 3055–3058.
[18] F. T. Edelmann, *Lanthanoids and Actinides*, in: *Synthetic Methods of Organometallic and Inorganic Chemistry (Hermann/Brauer)* (Ed.: W. A. Hermann), Thieme Medical Publishers, New York, **1997**, *6*, pp. 40.
[19] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999** *32*, 115–119.
[20] *SHELX97* Programs for Crystal Structure Analysis (Release 97–2). G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, Germany, **1998**.
[21] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
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