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# Lanthanide Complexes Coordinated by a Dianionic Bis(amidinate) Ligand with a Rigid Naphthalene Linker

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**Keywords:** Lanthanides / Amidinates / Coordination modes / Ligand design

The synthetic pathway to a new bis(amidine) ligand with a conformationally rigid naphthalene linker, 1,8-$C_{10}H_6$[NHC-(*t*Bu)=N(2,6-$Me_2$–$C_6H_3$)][N=C(*t*Bu)NH(2,6-$Me_2$–$C_6H_3$)] (**3**) was elaborated. Deprotonation of this bis(amidine) ligand with two equivalents of *n*BuLi and subsequent reaction with anhydrous $LnCl_3$ (Ln = Y, Nd, Sm) allowed the synthesis of the chlorido complexes [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$}$_2$]YCl(dme) (**4**), [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$}$_2$]Nd(dme)(μ-Cl)$_2$Li(dme) (**5**), and [1,8-$C_{10}H_6${NC(*t*Bu)-N-2,6-$Me_2$–$C_6H_3$}$_2$]Sm(thf)(μ-Cl)$_2$Li(thf)$_2$ (**6**), which are coordinated by the linked dianionic bis(amidinate) ligand. The structures of complexes **4**–**6** were established by X-ray diffraction studies, which reveal that the new ligand framework can coordinate to the lanthanide atoms in different fashions depending on the central atom ion size. Alkylation of complex **6** with equimolar amounts of $LiCH_2SiMe_3$ afforded the unexpected amido–amidinate complex [{1,8-$C_{10}H_6$(NC(*t*Bu)-N-2,6-$Me_2$–$C_6H_3$)$_2$}{1,8-$C_{10}H_6$(NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$)-(NH)}Sm][Li(dme)$_3$] (**7**), which obviously results from the cleavage of one amidinate group during decomposition of the transient alkyl species and ligand redistribution.

## Introduction

The amidinate ligands $[RC(NR')_2]^-$ belong to the group of four-electron chelating monoanionic ligands in which the negative charge is delocalized in the NCN fragment. Amidinates have proven to be versatile ligands because of the fact that their steric and electronic properties can easily be modified through variations of the organic substituents on the nitrogen atoms. The combination of flexibility and variety of coordination modes of amidinate ligands with donor properties results in their compatibility with a wide number of metal ions across the periodic table[1] and their suitability as a supporting ligand framework, which allows control over the metal atom coordination sphere and metal-mediated chemical processes. Application of amidinate ligands, which were introduced in the organometallic chemistry of rare-earth metals by Edelmann[2] and Teuben,[3] greatly influenced the development of this area and allowed the synthesis and characterization of a new series of isolable, highly reactive species. Monoalkyl, bis(alkyl), cationic alkyl, and hydrido rare-earth complexes supported by amidinate ligands have been described, and some of them demonstrated catalytic potential in reactions of transformation of unsaturated substrates (olefin polymerization,[3d,e;4] isoprene polymerization,[5] acetylene dimerization,[3c] olefin hydroboration,[6] hydrosilylation,[7] and hydroamination[8]). The stability and reactivity of rare-earth organometallic compounds are known to be largely determined by the degree of saturation of the coordination sphere of metal atom; therefore in recent years, the trend was toward the development of new ancillary ligands, which would allow greater flexibility in the design of the metal coordination environment.[9] Greater stability of rare-earth complexes can be achieved by use of more sterically hindered ligands or ligands that can give additional electronic stabilization to highly electronically unsaturated metal centers. Thus, employment of bulky amidinate ligands[3d,e;5;7] and amidinates containing an additional donor group[10] in the side chain allows to overcome the limitations inherent to the initially used *N*,*N'*-bis(trimethylsilyl)benzamidinate ligand and to synthesize the formerly inaccessible bis(alkyl) rare-earth species. Dianionic linked bis(amidinate) ligands[11] are highly interesting from the point of view of design and control of the geometry of the metal coordination sphere, and their use can stimulate progress in lanthanide chemistry similar to that observed by the transposition from metallocene to ansa-metallocene-type structures. Several examples of lanthanide complexes coordinated by linked bis(amidinate) ligands with flexible backbones have been reported.[12] In order to provide control of the geometry of the metal coordination sphere and control of the selectivity of the catalytic reactions mediated by metal complexes, we focused

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on elaboration of a new bulky bis(amidinate) ligand framework containing a rigid 1,8-disubstituted naphthalene linker. Herein, we report on the synthesis of a new linked bis(amidine) ligand, 1,8-$C_{10}H_6$[NHC(*t*Bu)=N(2,6-$Me_2$–$C_6H_3$)][N=C(*t*Bu)NH(2,6-$Me_2$–$C_6H_3$)], and its application for the preparation of lanthanide bis(amidinate) complexes.

## Results and Discussion

### Synthesis of 1,8-$C_{10}H_6$[NHC(*t*Bu)=N(2,6-$Me_2$–$C_6H_3$)]-[N=C(*t*Bu)NH(2,6-$Me_2$–$C_6H_3$)] (3)

1,8-Diaminonaphthalene was used as a platform for the synthesis of bis(amidine) ligand containing a conformationally rigid planar linker between two functional groups. The general procedure was based on those previously reported by Arnold[11a] and Hill[11c] that use pivaloyl chloride to give a tertiary butyl group at the amidine C functionality. The synthetic route is shown in Scheme 1. Synthesis of bis(amide) **1** proceeded easily by reacting 1,8-diaminonaphthalene with pivaloyl chloride in the presence of triethylamine in $CH_2Cl_2$; compound **1** was obtained in a 77% yield. Conversion of bis(amide) **1** to bis(imidoylchloride) **2** was achieved by addition of $PCl_5$ to a solution of **1** in chlorobenzene. In contrast to previously published synthetic procedures,[11a,11c] at this step, chlorobenzene was used instead of toluene in order to solubilize **1**. By heating the reaction mixture at 65 °C for 3 d, a yield of 42% was achieved. Extension of the reaction time to up to 5 d does not result in an increase in the product yield. The bis(amidine) **3** was synthesized by reaction of 2,6-dimethylaniline with **2** in chlorobenzene (65 °C, 3 d). Recrystallization of **3** from a $CH_2Cl_2$/hexane mixture allowed its isolation in a 70% yield as a pale-yellow crystalline solid, while when acetonitrile was used as the solvent, the solvate **3**·(MeCN) was obtained (63% yield). Products **1**–**3** returned acceptable microanalytical results.

Pale-yellow crystals of the bis(amidine) **3** suitable for X-ray diffraction studies were obtained by slow concentration of its solutions in $CH_2Cl_2$/hexane mixture (**3**) or in acetonitrile [**3**·(MeCN)] at room temperature. The molecular structure of **3** is shown in Figure 1, and the structure refinement data are listed in Table 1 [for the structure of **3**·(MeCN), see Supporting Information].

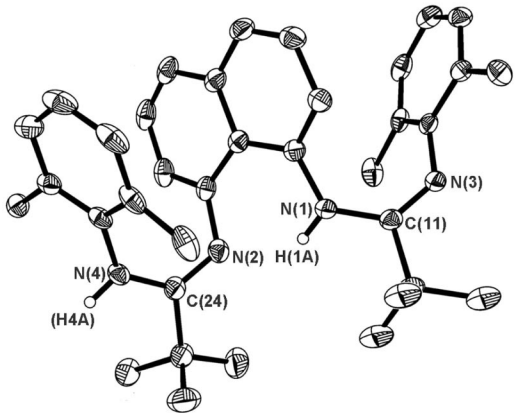
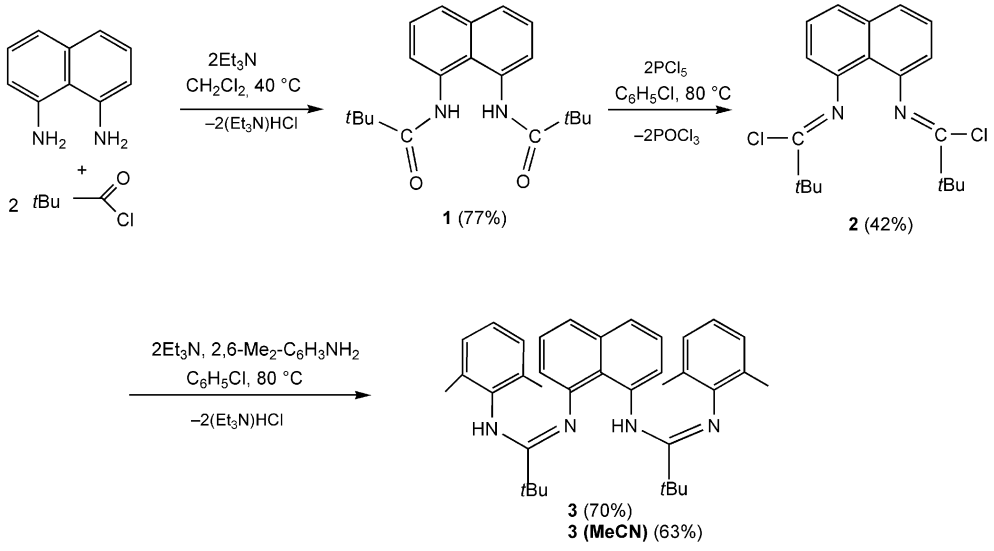



Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of **3**. Hydrogen atoms (except those of the amidine fragments) are omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)–C(1) 1.404(3), N(1)–C(11) 1.390(3), N(2)–C(3) 1.416(3), N(2)–C(24) 1.295(3), N(3)–C(11) 1.280(3), N(3)–C(16) 1.402(3), N(4)–C(24) 1.369(3), N(4)–C(29) 1.425(3), N(1)–C(11)–N(3) 128.3(2), C(11)–N(3)–C(16) 127.3(2), N(2)–C(24)–N(4) 126.7(2), C(24)–N(4)–C(29) 128.5(2).

The X-ray diffraction study reveals that bis(amidine) **3** can adopt conformations with different mutual arrangements of the amidine groups relative to the naphthalene fragment. Thus, in **3**, the amidine groups are situated in an *anti* position, while in **3**·(MeCN), they are in a *syn* position with respect to the naphthalene ring. The C(29–34) and C(2–7) rings in **3** are located in a "face to face" fashion, with a value of 22.2° for the dihedral angle between their




Scheme 1.

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Table 1. Crystallographic data and structure refinement details for **3**–**7**.

| | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|
| Empirical formula | $C_{36}H_{44}N_4$ | $C_{40}H_{52}ClN_4O_2Y$ | $C_{52}H_{82}Cl_2LiN_4NdO_6$ | $C_{48}H_{66}Cl_2LiN_4O_3Sm$ | $C_{71}H_{97}LiN_7O_6Sm$ |
| Formula weight | 532.75 | 745.22 | 1081.30 | 975.24 | 1301.85 |
| Crystal size [mm] | 0.50 × 0.50 × 0.40 | 0.40 × 0.40 × 0.27 | 0.26 × 0.15 × 0.07 | 0.28 × 0.15 × 0.09 | 0.40 × 0.12 × 0.10 |
| Space group | *Pbca* | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| *a* [Å] | 15.715(2) | 14.3924(4) | 28.2427(14) | 13.1746(3) | 15.7262(3) |
| *b* [Å] | 13.885(2) | 13.7686(4) | 17.7600(9) | 14.6174(3) | 19.3451(4) |
| *c* [Å] | 28.972(4) | 20.4216(6) | 22.1877(11) | 24.3385(6) | 22.3292(5) |
| *α* [°] | 90 | 90 | 90 | 93.4900(10) | 90 |
| *β* [°] | 90 | 107.6570(10) | 96.0580(10) | 92.0370(10) | 97.1330(10) |
| *γ* [°] | 90 | 90 | 90 | 93.2970(10) | 90 |
| *V* [Å$^3$] | 6322.1(16) | 3856.16(19) | 11067.0(10) | 4667.05(18) | 6740.5(2) |
| *Z* | 8 | 4 | 8 | 4 | 4 |
| Calculated density [mg/m$^3$] | 1.119 | 1.284 | 1.298 | 1.388 | 1.283 |
| *μ* [mm$^{-1}$] | 0.066 | 1.620 | 1.083 | 1.417 | 0.926 |
| $T_{min}/T_{max}$ | 0.9679/0.9710 | 0.5635/0.6689 | 0.7660/0.9280 | 0.6925/0.8831 | 0.7082/0.9131 |
| *F*(000) | 2304 | 1568 | 4536 | 2020 | 2740 |
| 2*θ* [°] | 52 | 52 | 53 | 55 | 52 |
| Unique reflections collected ($R_{int}$) | 6202 (0.0448) | 7541 (0.0281) | 22872 (0.0536) | 21191 (0.0175) | 57778 (0.0436) |
| $R_1$ [$I > 2\sigma(I)$] | 0.0649 | 0.0331 | 0.0650 | 0.0331 | 0.0377 |
| $wR_2$ (all data) | 0.1801 | 0.0861 | 0.1692 | 0.0875 | 0.0980 |
| Parameters | 380 | 445 | 1111 | 1063 | 800 |
| Goodness-of-fit on $F_2$ | 1.031 | 1.046 | 1.046 | 1.060 | 1.050 |
| Largest diff. hole and peak /e/Å$^3$ | –0.612/0.685 | –0.240/1.078 | –1.286/2.472 | –0.825/1.940 | –0.544/1.676 |

planes. The short distance between the centers of these rings (3.473 Å) allows for the realization of π–π interactions[13] in **3**.

Unlike in previously reported linked bis(amidine) groups,[11a,11c] in both **3** and **3**·(MeCN), the hydrogen atoms in the amidine groups are attached to different nitrogen atoms. This fact becomes evident from analysis of the geometric parameters of the amidine groups. Within one of the two NCN fragments, the bond length N($C_{10}H_6$)–C [1.292(2) Å] is comparable to that of a normal double C=N bond,[14] while the bond between central carbon atom and the nitrogen atom of the 2,6-dimethylaniline moiety is substantially longer [1.371(2) Å] and corresponds better to a single N–C bond. In the second NCN fragment, the bonding situation is reverse: the bond N($C_{10}H_6$)–C is long [1.414(2) Å] and the C–N(2,6-$Me_2$–$C_6H_3$) is short [1.272(2) Å]. It should be noted that intramolecular N···H hydrogen bonds are realized in **3** and **3**·(MeCN). The N(2)···H(1A) and N(1)···H(2A) distances in **3** and **3**·(MeCN) are 2.10(2) and 2.02(2) Å, respectively. The NHN bond angles at the hydrogen atoms are 138.9(3)° in **3** and 135.1(4)° in **3**·(MeCN). The different locations of the hydrogen atoms within the two amidine fragments is proved also by the solid-state IR spectrum of **3**: the NH groups give rise to two different absorption bands at 3400 and 3278 cm$^{-1}$. Obviously, the same situation is retained in solution since the protons attached to the nitrogen atoms in the $^1$H NMR spectrum of **3** give rise to a set of two singlets of equal intensity at $\delta$ = 6.07 and 8.98 ppm.

In order to evaluate the difference in the energies of the conformers and the energy of the intramolecular N···H hydrogen bonds, density functional theory (DZVP basis set) calculations on the isolated molecules **3** and **3**·(MeCN) were carried out with the program Firefly 71c.[15] According to these calculations, the conformation that is realized in complex **3** is energetically preferable (1.18 kcal/mol) relative to that of **3**·(MeCN). Probably stabilization of the conformation of **3**·(MeCN) is reached because of the presence of solvate molecules of MeCN in the crystal. In order to evaluate the energy of the intramolecular N···H hydrogen bonds, the Bader theory[16] and the correlation equation of Espinosa[17] were used. The calculations have shown that the energy of the bonds N(2)···H(1A) and N(1)···H(2A) in **3** and **3**·(MeCN) are 9.68 and 9.93 kcal/mol, respectively.

### Synthesis of Bis(amidinate)Chlorido Lanthanide Complexes

Bis(amidine) **3** can easily be deprotonated by treatment with 2 equiv. of *n*BuLi in a thf/hexane mixture at 0 °C. The dilithium derivative of **3** obtained after metallation with *n*BuLi was used in situ in the reaction with anhydrous $LnCl_3$ (Ln = Y, Nd, Sm; 1:1 molar ratio) in thf at ambient temperature (Scheme 2).

Evaporation of thf, extraction of the solid residue with toluene, and subsequent recrystallization of the reaction product from dme/hexane (**4**), diethyl ether (**5**), or thf/hexane (**6**) mixtures led to the isolation of bis(amidinate)-chlorido lanthanide complexes [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$}$_2$]YCl(dme) (**4**), [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$}$_2$]Nd(dme)(μ-Cl)$_2$Li(dme) (**5**), and [1,8-$C_{10}H_6$-{NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$}$_2$]Sm(thf)(μ-Cl)$_2$Li(thf)$_2$ (**6**) in reasonable yields (45–61%). Complexes **4**–**6** were obtained as pale-yellow crystalline moisture- and air-sensitive solids. They are soluble in thf, dme, $Et_2O$, and toluene and are slightly soluble in hexane. The $^1$H and $^{13}$C{$^1$H}NMR spectra of the diamagnetic yttrium derivative **4** in $C_6D_6$ at 20 °C show the expected set of signals corresponding to the bis-

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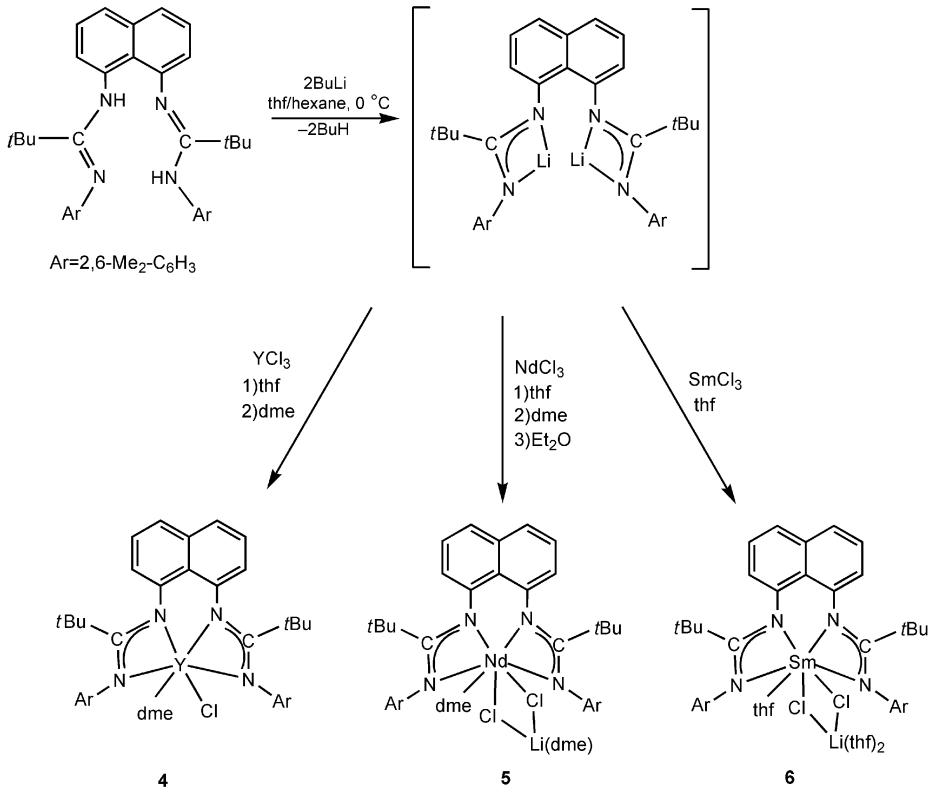


Scheme 2.

(amidinate) ligand and the dme molecule. The protons of the *t*Bu groups give rise to a single singlet at $\delta$ = 0.88 ppm, and the protons of the xylyl fragments appear as a singlet at $\delta$ = 2.46 ppm. Two broad singlets at $\delta$ = 2.67 and 2.99 ppm correspond to the methyl and methylene protons of the dme molecules. The variable-temperature $^1$H and $^{13}$C{$^1$H} NMR spectroscopic data for **4** is indicative of complex dynamic behavior over the temperature range +60 to –60 °C (in $C_7D_8$), which results in an apparent mirror plane within the molecule. Clear pale-yellow crystals of complexes **4**–**6** suitable for X-ray diffraction studies were obtained by slow concentration of their solutions (**4**: dme/hexane mixture, **5**: diethyl ether, **6**: thf/hexane mixture) at ambient temperature. Complex **5** was isolated as a solvate **5**·($2Et_2O$), while the crystals of **4** and **6** do not contain solvent molecules. Crystals of complexes **5** and **6** contain two crystallographically independent molecules. The molecular structures of **4**–**6** are shown in Figures 2, 3, and 4, respectively; the structure refinement data are listed in Table 1. X-ray diffraction studies reveal that compound **4** is a monomeric salt-free complex, while **5** and **6** are heterobimetallic complexes. The coordination sphere of the yttrium atom in **4** is made up of four nitrogen atoms of two amidinate fragments, two oxygen atoms of the dme molecule, and one terminal chlorido ligand. In complexes **5** and **6**, the coordination spheres of the metal atoms contain two chlorine atoms that μ-bridge the lanthanide and lithium atoms, in addition to four nitrogen atoms of the bis(amidinate) ligand and the oxygen atoms of coordinated Lewis bases (**5**: two oxygen atoms of the dme molecule, **6**: one oxygen atom of the thf molecule). The lithium atom in **5** is coordinated by one dme molecule and in complex **6** by two thf molecules. The four Ln–N distances in compounds **4**–**6** have rather similar values [**4**: 2.331(1)–2.369(1); **5**: 2.454(3)–2.573(3); **6**: 2.404(2)–2.481(2) Å], and the average bond lengths are comparable to those reported for related bis(amidinate) complexes (Y,[3a,12a] Nd,[2c] Sm[18]).

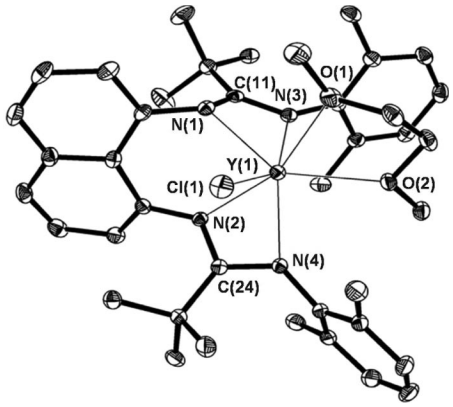


Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y(1)–N(1) 2.331(1), Y(1)–N(4) 2.348(1), Y(1)–N(3) 2.354(1), Y(1)–N(2) 2.369(1), Y(1)–O(1) 2.409(1), Y(1)–O(2) 2.421(1), Y(1)–Cl(1) 2.596(4), N(1)–C(11) 1.348(2), N(2)–C(24) 1.341(2), N(3)–C(11) 1.328(2), N(4)–C(24) 1.354(2), N(1)–Y(1)–N(3) 56.17(5), N(4)–Y(1)–N(2) 55.88(4).

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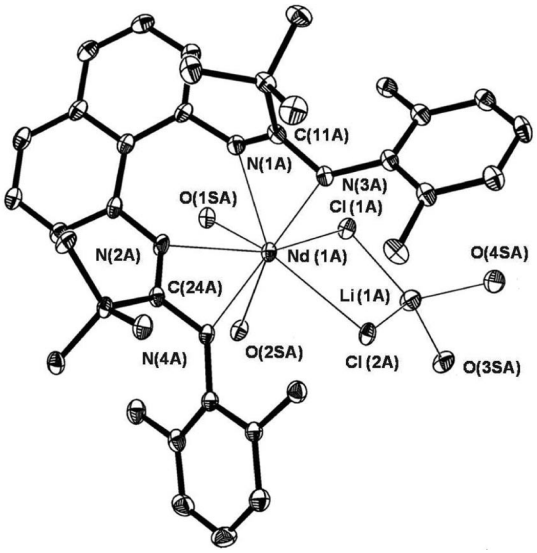


Figure 3. ORTEP diagram (30% probability thermal ellipsoids) of **5**. Hydrogen atoms and methyl and methylene groups of the dme molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Nd(1A)–N(2A) 2.454(3), Nd(1A)–N(1A) 2.479(3), Nd(1A)–N(3A) 2.496(3), Nd(1A)–O(1SA) 2.555(2), Nd(1A)–N(4A) 2.573(3), Nd(1A)–O(2SA) 2.602(2), Nd(1A)–Cl(2A) 2.8056(9), Nd(1A)–Cl(1A) 2.8869(9), N(1A)–C(11A) 1.320(5), N(2A)–C(24A) 1.334(5), N(3A)–C(11A) 1.339(5), N(4A)–C(24A) 1.330(4), Cl(1A)–Li(1A) 2.287(7), Cl(2A)–Li(1A) 2.318(7), Li(1A)–O(4SA) 1.947(8), Li(1A)–O(3SA) 2.015(8), N(1A)–Nd(1A)–N(3A) 52.7(1), N(2A)–Nd(1A)–N(4A)51.8(1).

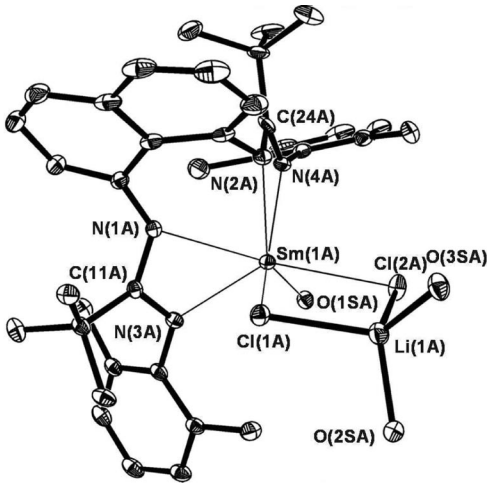


Figure 4. ORTEP diagram (30% probability thermal ellipsoids) of **6**. Hydrogen atoms and the methylene groups of the thf molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm(1A)–N(2A) 2.404(2), Sm(1A)–N(4A) 2.415(2), Sm(1A)–N(3A) 2.419(2), Sm(1A)–N(1A) 2.481(2), Sm(1A)–O(1SA) 2.576(2), Sm(1A)–Cl(2A) 2.7611(7), Sm(1A)–Cl(1A) 2.7675(6), Cl(1A)–Li(1A) 2.328(5), Cl(2A)–Li(1A) 2.326(5), N(1A)–C(11A)1.327(3), N(2A)–C(24A)1.358(3), N(3A)–C(11A) 1.359(3), N(4A)–C(24A) 1.338(3), N(2A)–Sm(1A)–N(4A) 54.52(7), N(3A)–Sm(1A)–N(1A) 53.62(7).

The bonding situation within the NCN fragments of complexes **4**–**6** indicates a negative charge delocalization. Comparison of the structures of complexes **4**–**6** reveals versatility of the coordination modes of the new bis(amidinate) ligand framework to the lanthanide atoms, which is dependent on ion size of the central atom. Thus, in complexes of yttrium and samarium, the amidinate groups are located in a *trans* position with respect to the naphthalene fragment, while in the neodymium derivative with a larger ion,[19] they adopt a *cis* configuration (Figure 5). At the same time, the values of the dihedral angles in these cases differ substantially: in complexes **4** and **6** they are in the region 77.6–79.7°, while in complex **5** this value is much larger – 109.4 and 109.6°. Moreover, the coordination of bis(amidine) **3** to lanthanide atoms of different sizes provokes distortions of different magnitudes in the naphthalene linker. In parent bis(amidine) **3**, the mean deviation of the carbon atoms of the naphthalene ring from the plane is 0.0483 Å [0.0505 Å for **3**·(MeCN)]. However, the same parameter in complexes **4** and **6**, which display a *trans* disposition of the amidinate groups, has values of 0.1119 Å and 0.1069, 0.1016 Å respectively. In complex **5**, where the amidinate groups are located on the same side of the naphthalene ring the value of mean deviation (0.0461, 0.0459 Å) is noticeably lower and is similar to that observed for starting bis(amidine) **3**. The attempt to alkylate complex **6** with an equimolar amount of $LiCH_2SiMe_3$ was carried out in toluene at 0 °C. Separation of the precipitate of LiCl, evaporation of toluene in vacuo, and subsequent recrystallization of the solid residue from a

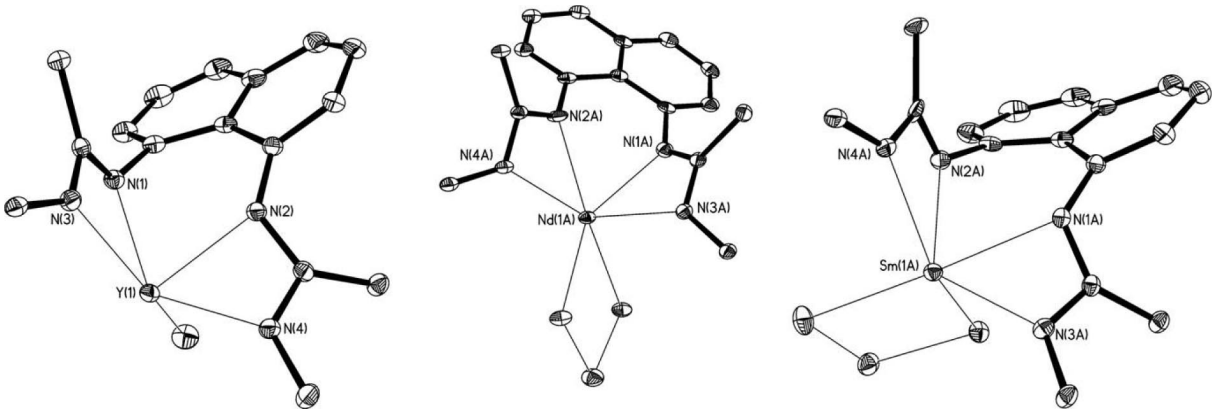


Figure 5. Dihedral angles between planes N(3)LnN(1) and N(2)LnN(4) in complexes **4**–**6** (**4**: 77.6°; **5**: 109.4, 109.6°; **6**: 78.5, 79.7°).

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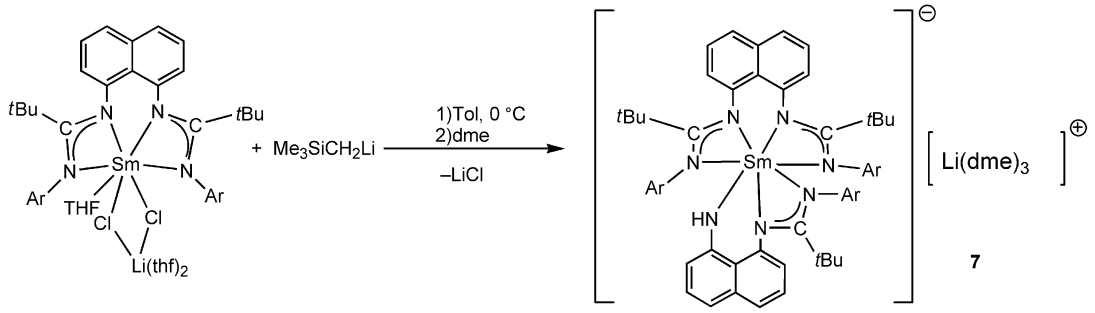


Scheme 3.

dme/hexane mixture led to the isolation of an unexpected product [{1,8-$C_{10}H_6$(NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$)$_2$}{1,8-$C_{10}H_6$(NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$)(NH)}Sm][Li(dme)$_3$] (**7**) (Scheme 3). All attempts to isolate other samarium-containing products failed. Complex **7** was obtained as a yellow crystalline moisture- and air-sensitive solid in 24% yield. Complex **7** is soluble in thf, dme, $Et_2O$, and toluene and insoluble in hexane. Transparent yellow crystals of **7** suitable for X-ray single-crystal structure investigation were obtained by slow concentration of the solution in a dme/hexane mixture at ambient temperature. The X-ray diffraction study reveals that complex **7** is an ionic compound (Figure 6) consisting of the complex anion formed by the $Sm^{3+}$ cation coordinated to one dianionic bis(amidinate) ligand and one dianionicamido–amidinate ligand {1,8-$C_{10}H_6$(NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$)(NH)}$^{2-}$. The coordination sphere of the samarium atom in **7** is made up of seven nitrogen atoms, thus providing a formal coordination number of seven. The formation of **7** obviously results from the cleavage of one amidinate fragment during decomposition of the transient alkyl complex and ligand redistribution. The cationic part consists of the Li cation coordinated to three dme molecules. The average Sm–N(amidinate) bond length in **7** [2.470(2) Å] is somewhat longer than those in the parent complex of the seven-coordinate samarium **6** [2.429(2) Å] and ionic bis(guanidinate) complexes [($Me_3Si$)$_2$NC(N-R)$_2$]$_2$-Sm-(μ-$BH_4$)$_2$Li(thf)$_2$ (R = Cy, 2.424 Å;[20] R = *i*Pr, 2.455 Å[21]). The Sm–N(amido) bond length [2.350(2) Å] in **7** is similar to that formerly reported for a related ionic amido complex {Li(thf)$_4$}{Sm[(*R*)-$C_{20}H_{12}N_2$($C_{10}H_{22}$)]$_2$} [2.348(3) Å].[22]

Further studies on the synthesis of alkyl, hydrido, borohydride, alkoxide, and amido species supported by new linked bis(amidinate) ligand systems are currently in progress.

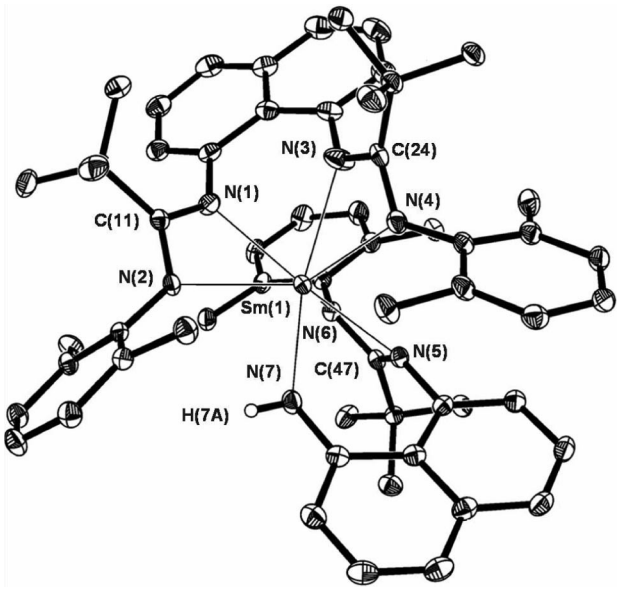


Figure 6. ORTEP diagram (30% probability thermal ellipsoids) of the anionic part of **7**. Hydrogen atoms (except that of the amido group) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm(1)–N(7) 2.350(2), Sm(1)–N(6) 2.420(2), Sm(1)–N(5) 2.434(2), Sm(1)–N(3) 2.473(2), Sm(1)–N(1) 2.476(2), Sm(1)–N(4) 2.483(2), Sm(1)–N(2) 2.538(2), N(7)–Sm(1)–N(6) 100.72(7), N(7)–Sm(1)–N(5) 69.49(7), N(6)–Sm(1)–N(5) 54.50(6), N(1)–Sm(1)–N(2) 52.17(6), N(3)–Sm(1)–N(4) 52.56(7).

## Conclusions

A new dianionic bis(amidinate) ligand framework with a conformationally rigid naphthalene linker was developed and shown to form a suitable coordination environment for lanthanide ions. The salt metathesis reactions of dilithium derivatives of **3** with $LnCl_3$ (Ln = Y, Nd, Sm) for the metals with a small ion size (Y) results in the synthesis of monomeric salt-free bis(amidinate)chlorido complexes, while for the metals possessing larger ion sizes (Nd, Sm), the formation of heterobimetallic complexes was observed. The structures of complexes **4**–**6** were established by X-ray diffraction studies, which reveal that a new ligand framework can coordinate to lanthanide atoms in different fashions depending on the central atom ion size. The attempt to synthesize a samarium alkyl species that is supported by the linked bis(amidinate) ligand by reaction of complex **6** with an equimolar amount of $LiCH_2SiMe_3$ afforded the unexpected amido–amidinate complex **7**, which obviously was formed by cleavage of one amidinate group during decomposition of the transient alkyl species and ligand redistribution.

## Experimental Section

All experiments were performed in evacuated tubes by using standard Schlenk techniques, with the rigorous exclusion of traces of

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moisture and air. After drying over KOH, thf was purified by distillation from sodium/benzophenone ketyl and hexane and toluene by distillation from sodium/triglyme benzophenone ketyl prior to use. $C_6D_6$ was dried with sodium/benzophenone ketyl and condensed in vacuo prior to use. $CH_2Cl_2$ and $C_6H_5Cl$ were dried with $P_2O_5$, distilled twice, and degassed by freeze-vacuum-thaw cycles prior to use. 1,8-diaminonaphthalene and pivaloyl chloride were purchased from Acros. Anhydrous $YCl_3$, $SmCl_3$, $NdCl_3$,[23] and $Me_3SiCH_2Li$[24] were prepared according to literature procedures. All other commercially available chemicals were used after appropriate purification. NMR spectra were recorded on Bruker Avance DRX-400 and DPX-200 spectrometers in $C_6D_6$ or $CDCl_3$ at 20 °C, unless otherwise stated. Chemical shifts for $^1H$ and $^{13}C$ spectra were referenced internally by using the residual solvent resonances and are reported relative to tms in parts per million (ppm). IR spectra were recorded as Nujol mulls on a "Bruker-Vertex 70" instrument. Lanthanide metal analyses were carried out by complexometric titration. Mass spectra were recorded on a Polaris Q/Trace GC Ultra (Ion Trap analyser) chromatography mass spectrometer. The C, H, N elemental analysis was performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

**1,8-$C_{10}H_6${NHC(O)*t*Bu}$_2$ (1):** Pivaloyl chloride (3.15 g, 26.20 mmol) was added slowly to a solution of 1,8-diaminonaphthalene (2.00 g, 12.65 mmol) and $Et_3N$ (2.65 g, 26.23 mmol) in $CH_2Cl_2$ (30 mL) at room temperature to give an exothermic reaction. The reaction mixture was stirred at 35 °C for 16 h, and the volatiles were removed in vacuo at room temperature. After trituration with water (3× 50 mL), the grey solid was washed with hexane (3× 50 mL) and dried in vacuo at room temperature for 2 h. Yield: 3.16 g (77%). $C_{20}H_{26}N_2O_2$ (326.4): calcd. C 73.69, H 8.03, N 8.58; found C 73.25, H 8.29, N 8.15. $^1H$ NMR (200 MHz, $C_5D_5N$, 20 °C): $\delta$ = 1.46 (s, 18 H, $CMe_3$), 7.36–8.71 (m, 6 H, aryl), 10.34 (br. s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $C_5D_5N$, 20 °C): $\delta$ = 27.6 [s, C($C$H$_3$)], 40.0 [s, $C$(CH$_3$)], 123.5, 123.6, 124.6, 124.7, 126.7, 136.2 (s, C aryl), 179.263 (C=O) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3374 (s, NH), 3065 (w, aryl), 1655 (s, C=O), 1580 (m), 1498 (s), 1278 (m), 1252 (w), 1231 (m), 1192 (m), 1169 (m), 1034 (m), 940 (m), 833 (m), 808 (m) cm$^{-1}$. MS (EI): $m/z$ = 326.2 [M$^+$].

**1,8-$C_{10}H_6${N=C(Cl)*t*Bu}$_2$ (2):** $PCl_5$ (3.30 g, 15.80 mmol) was added in portions to a solution of **1** (2.60 g, 7.90 mmol) in chlorobenzene (30 mL) in vacuo to give a cloudy, green solution, which was stirred at 65 °C for 3 d. The solution was filtered, the volatiles were removed in vacuo at room temperature, and the solid residual was extracted with hexane (2× 20 mL). The hexane extracts were filtered, slowly concentrated in vacuo at room temperature to half of the initial volume, and left overnight at 0 °C. The mother liquor was separated by decantation and the pale-yellow crystalline solid was washed with cold hexane (15 mL) and dried in vacuo at room temperature for 40 min to yield 1.20 g (42%) of **2**. $C_{20}H_{24}Cl_2N_2$ (363.4): calcd. C 66.12, H 6.66, Cl 19.52, N 7.71; found C 66.01, H 6.35, Cl 19.05, N 7.43. $^1H$ NMR (200 MHz, $CDCl_3$, 20 °C): $\delta$ = 1.46 (s, 18 H, $CMe_3$), 6.62–7.69 (m, 6 H, aryl) ppm. $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$, 20 °C): $\delta$ = 27.1 [C($C$H$_3$)], 27.6 [C($C$H$_3$)], 39.9 [$C$(CH$_3$)], 124.1, 124.4, 125.6, 127.4, 132.9, 136.1 (s, C aryl), 179.2 (N=$C$) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3050 (w), 1673 (s, N=C), 1611 (w), 1569 (s), 1477 (m), 1327 (m), 1263 (m), 1210 (s), 1033.9 (m), 934 (s), 835 (s), 808 (s), 791 (m), 760 (s) cm$^{-1}$.

**1,8-$C_{10}H_6$[NHC(*t*Bu)=N(2,6-Me$_2$–C$_6$H$_3$)][N=C(*t*Bu)NH(2,6-Me$_2$–C$_6$H$_3$)] (3):** 2,6-Dimethylaniline (1.53 g, 12.70 mmol) was added in portions to a solution of **2** (2.00 g, 5.52 mmol) in chlorobenzene (30 mL) in vacuo to give a yellow solution. The reaction mixture was stirred at 65 °C for 3 d, and the volatiles were removed in vacuo to yield a pale-yellow solid. $Et_2O$ (50 mL) and an aqueous solution of $Na_2CO_3$ (50 mL, 0.5 M) were added to the residual solid, and the mixture was stirred for 30 min. The organic layer was separated, washed with water (3× 20 mL) and dried with $MgSO_4$. The solvent was removed in vacuo at room temperature to give a yellow solid. Recrystallization of the residue from a mixture of hexane/$CH_2Cl_2$ (2:1) afforded **3** as pale-yellow crystals (2.94 g, 70%). If **3** was recrystallized from acetonitrile, pale-yellow crystals of **3**·(**MeCN**) were obtained (2.65 g, 63%). $C_{36}H_{44}N_4$ (532.8): calcd. C 81.16, H 8.32, N 10.52; found C 81.42, H 8.00, N 10.31. $^1H$ NMR (200 MHz, $CDCl_3$, 20 °C): $\delta$ = 1.45 [s, 9 H, C(CH$_3$)$_3$], 1.55 [s, 9 H, C(CH$_3$)$_3$], 2.01 (s, 3 H, CH$_3$), 2.05 (s, 9 H, CH$_3$), 6.07 (s, 1 H, NH), 6.24–6.81 (m, 12 H, aryl), 8.99 (s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $C_6D_6$, 20 °C): $\delta$ = 18.5 (CH$_3$), 29.4 [C($C$H$_3$)$_3$], 39.6 [$C$(CH$_3$)$_3$], 40.4 [$C$(CH$_3$)$_3$], 113.3, 115.7, 120.0, 121.1, 122.5, 123.7, 124.1, 125.6, 127.6 (aryl, CH), 117.6, 127.4, 135.1, 135.8, 137.8, 147.0 (aryl, C), 159.3 (NCN), 162.4 (NCN) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3400 (m), 3278 (m, N–H), 3043 (w), 1638 (m, C=N), 1608 (w), 1570 (w), 1369 (w), 1288 (m), 1209 (w), 1135 (m), 1034 (w), 925 (w), 894 (m), 884 (m), 831 (m), 820 (m), 806 (m), 760 (s) cm$^{-1}$. MS (EI): $m/z$ = 532.3 [M$^+$].

**Synthesis of [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-Me$_2$–C$_6$H$_3$}$_2$]YCl(dme) (4):** A solution of *n*BuLi in hexane (2.18 mL, 0.95 N, 2.07 mmol) was added to a solution of **3** (0.55 g, 1.03 mmol) in thf (30 mL) at 0 °C; the reaction mixture was stirred for 40 min and was then slowly warmed up to 20 °C. $YCl_3$ (0.20 g, 1.03 mmol) was added, and the reaction mixture was stirred overnight. The solvent was evaporated in vacuo, and the solid residue was extracted with toluene (2× 20 mL). The toluene extracts were filtered, and the solvent was evaporated in vacuo. After recrystallization of the residue from a mixture of hexane/dme, pale-yellow crystals of **4** were obtained in a yield of 0.45 g (45%). $C_{40}H_{52}ClN_4O_2Y$ (745.3): calcd. C 64.47, H 7.03, Y 11.93; found C 64.21, H 6.85, Y 11.86. $^1H$ NMR (200 MHz, $C_6D_6$, 20 °C): $\delta$ = 0.88 [s, 18 H, C(CH$_3$)$_3$], 2.46 (s, 12 H, CH$_3$), 2.67 (br. s, 4 H, OCH$_2$, dme), 2.99 (br. s, 6 H, OCH$_3$, dme), 6.79–7.49 (m, 12 H, C-H aryl) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $C_6D_6$, 20 °C): $\delta$ = 20.1 (CH$_3$), 30.3 [C($C$H$_3$)$_3$], 42.9 [$C$(CH$_3$)$_3$], 61.2 (s, OCH$_3$, dme), 69.9 (s, OCH$_2$, dme), 120.5, 121.7, 122.1, 124.8, 128.0, 130.7, 135.7, 145.6, 148.7 (s, aryl), 179.9 (d, $^1J_{Y\text{-}C}$ = 2.4 Hz, NCN) ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3054 (w), 1673 (m), 1569 (m), 1503 (w), 1261 (w), 1218 (m), 1172 (m), 1091 (s), 1046 (s), 934 (w), 860 (s), 764 (s) cm$^{-1}$.

**[1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-Me$_2$–C$_6$H$_3$}$_2$]Nd(dme)(μ-Cl)$_2$Li(dme) (5):** A solution of *n*BuLi in hexane (6.13 mL, 0.79 N, 4.84 mmol) was added to a solution of **3** (1.29 g, 2.42 mmol) in thf (30 mL) at 0 °C; the reaction mixture was stirred for 40 min and was then slowly warmed up to 20 °C. $NdCl_3$ (0.61 g, 2.42 mmol) was added to the solution, and the reaction mixture was stirred overnight. Volatiles were removed in vacuo, and the remaining solid was extracted with toluene (2× 20 mL). The extracts were filtered, and toluene was removed in vacuo. The solid residue was treated with dme and recrystallized from diethyl ether. Pale-yellow crystals of **5** were obtained in a yield of 0.98 g (47%). $C_{52}H_{82}Cl_2LiN_4NdO_8$ (1113.4): calcd. C 56.10, H 7.42, Nd 5.03; found C 56.03, H 7.01, Nd 4.95. IR (Nujol, KBr): $\tilde{\nu}$ = 1590 (s), 1258 (m), 1122 (w), 1122 (w), 1047 (s), 931 (s), 861 (m), 890 (m), 806 (m), 759 (s) cm$^{-1}$.

**[1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-Me$_2$–C$_6$H$_3$}$_2$]Sm(thf)(μ-Cl)$_2$Li(thf)$_2$ (6):** A solution of *n*BuLi in hexane (1.56 mL, 1.08 N, 1.68 mmol) was added to a solution of **3** (0.45 g, 0.84 mmol) in thf (30 mL) at 0 °C; the reaction mixture was stirred for 40 min and was then slowly warmed up to 20 °C. $SmCl_3$ (0.22 g, 0.84 mmol) was added, and the

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reaction mixture was stirred overnight. The solvent was removed in vacuo, and the solid residue was extracted with toluene (2× 20 mL). The toluene extracts were filtered, and the solvent was removed in vacuo. Recrystallization of the residue from a hexane/thf mixture afforded pale-yellow crystals of **6** (0.50 g, 61%). $C_{48}H_{66}Cl_2LiN_4O_3Sm$ (975.4): calcd. C 59.11, H 6.82, Sm 15.42; found C 58.83, H 6.91, Sm 14.98. $^1$H NMR (200 MHz, $C_5D_5N$, 20 °C): $\delta$ = 1.54 [s, 9 H, $C(CH_3)_3$], 1.55 (br. s, 12 H, thf β-$CH_2$), 1.66 [s, 9 H, $C(CH_3)_3$], 2.16 (s, 12 H, $CH_3$), 3.60 (br. s, 12 H, thf α-$CH_2$), 6.49–8.56 (m, 12 H, C-H aryl) ppm. $^{13}$C{$^1$H} NMR (50 MHz, $C_5D_5N$, 20 °C): $\delta$ = 19.0 ($CH_3$), 26.0 (thf, β-$CH_2$) 29.5 [$C(CH_3)_3$], 29.8 [$C(CH_3)_3$], 40.2 [$C(CH_3)_3$], 41.0 [$C(CH_3)_3$], 67.9 (thf, α-$CH_2$), 113.4, 116.9, 118.2, 120.6, 121.6, 122.5, 124.6, 125.9, 127.9, 128.8, 129.5, 134.4, 137.3, 138.8, 146.7, 148.0 (s, aryl), 154.5 (s, NCN), 164.9 (s, NCN) ppm. $^7$Li NMR (78 MHz, $C_5D_5N$, 20 °C): $\delta$ = 5.4 ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3041 (w), 1638 (s), 1565 (m), 1566 (m), 1257 (m), 1223 (m), 1180 (m), 1113 (w), 1095 (s), 1053 (s), 1050 (m), 1030 (m), 929 (w), 775 (s), 764 (m) cm$^{-1}$.

**Reaction of [1,8-$C_{10}H_6${NC(*t*Bu)N-2,6-$Me_2$–$C_6H_3$}$_2$]Sm(thf)(μ-Cl)$_2$-Li(thf)$_2$ with $LiCH_2SiMe_3$. Synthesis of 7:** To a solution of **6** (0.38 g, 0.39 mmol) in toluene (20 mL) was slowly added a solution of $Me_3$-$SiCH_2Li$ (0.04 g, 0.47 mmol) in toluene (10 mL) at 0 °C, and the reaction mixture was stirred for 1 h. The yellow solution was filtered, the solvent was removed in vacuo, and the solid residue was recrystallized from a mixture of hexane/dme to give yellow crystals of **7** (0.12 g, 24%). $C_{72}H_{100}LiN_7O_6Sm$ (1316.1): calcd. C 65.67, H 7.65, Sm 11.42; found C 65.19, H 7.32, Sm 11.38. $^1$H NMR (400 MHz, $C_6D_6$, 20 °C): $\delta$ = 0.15 [br. s, 18 H, $C(CH_3)_3$], 0.42 [br. s, 9 H, $C(CH_3)_3$], 1.24 (br. s, 6 H, $CH_3$), 1.54 (br. s, 12 H, $CH_3$), 3.11 (br. s, 18 H, $OCH_3$, dme), 3.32 (br. s, 12 H, $OCH_2$, dme), 6.17–7.71 (m, 21 H, C-H aryl) ppm. $^{13}$C{$^1$H} NMR (50 MHz, $C_6D_6$, 20 °C): $\delta$ = –0.2 [$C(CH_3)_3$], 1.0 [$C(CH_3)_3$], 28.9 ($CH_3$), 29.7 ($CH_3$), 39.1 [$C(CH_3)_3$], 40.4 [$C(CH_3)_3$], 58.3 (s, $OCH_3$, dme), 71.9 (s, $OCH_2$, dme), 113.6, 114.7, 115.9, 116.7, 119.2, 120.4, 121.4, 122.1, 122.9, 123.7, 124.1, 124.3, 126.1, 127.0, 127.2, 128.5, 129.7, 133.4, 135.4, 137.4 (s, CH aryl), 157.1, 158.7, 162.2 (NCN) ppm. $^7$Li NMR (156 MHz, $C_6D_6$, 20 °C): $\delta$ = 6.0 ppm. IR (Nujol, KBr): $\tilde{\nu}$ = 3289 (w), 3038 (w), 1638 (s), 1608 (m), 1570 (w), 1291 (m), 1262 (m), 1156 (w), 1035 (m), 963 (m), 820 (s) cm$^{-1}$.

**X-ray Crystallography:** The data were collected on a SMART APEX diffractometer (graphite-monochromated, Mo-$K_\alpha$ radiation, $\omega$- and $\theta$-scan technique, $\lambda$ = 0.71073 Å) at 100 K. The structures were solved by direct methods and were refined on $F^2$ by using the SHELXTL[25] package. All non-hydrogen atoms were refined anisotropically. The NH hydrogen atoms in **3**, **3**·(MeCN) and **7** were found from Fourier syntheses of electron density and were refined isotropically, whereas the other H atoms in **3**–**7** were placed in calculated positions and were refined in the riding model. SADABS[26] was used to perform the area-detector scaling and absorption corrections. CCDC-753381 (**3**), -753382 [**3**·(MeCN)], -753383 (**4**), -753384 (**5**), -753385 (**6**), and -753386 (**7**) 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.

**DFT Calculations:** The theoretical study of **3** and **3**·(MeCN) was performed at the density functional theory (DFT) level with the hybrid B3LYP functional by using the DZVP basis set and the program PC-Gamess (Firefly 71c).[15] The absence of imaginary frequencies shows that the molecules are in a minimum for the potential energy. The AIMALL[27] program was used to search for critical points and for the calculation of the hydrogen bond energy.

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