Lanthanide(III) Amidinates with Six- and Seven-Coordinate Metal Atoms

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Dedicated to Professor Uwe Klingebiel on the Occasion of his 60th Birthday

Abstract. The crystalline lithium *N,N′*-diorganoamidinates Li[PhC(NR)$_2$] (**1**: R = *c*-C_6H_{11}, **2**: R = *i*Pr) and Li[$(CF_3)_3C_6H_2C$-(N-*c*-$C_6H_{11})_2$] (**3**) have been obtained by the reaction of phenyllithium or 2,4,6-tris(trifluoromethyl)phenyllithium, resp., with diorganocarbodiimides R-N=C=N-R (R = *c*-C_6H_{11}, *i*Pr). These amidinates have been used for the synthesis of the homoleptic lanthanide(III) amidinates [PhC(N-*c*-$C_6H_{11})_2]_3$Ln (**4−6**: Ln = Pr, Nd, Sm) and [PhC(N*i*Pr)$_2]_3$Pr (**7**). Seven-coordinate Lewis-base adducts of the type [PhC($NSiMe_3)_2]_3$Ln(NCPh) (**8,9**: Ln = Sm, Eu) have been prepared by addition of benzonitrile to the homoleptic precursors [PhC($NSiMe_3)_2]_3$Ln. The compounds **2** (as its THF adduct), **4**, **6**, **8** and **9** have been structurally characterized by single crystal X-ray analyses.

Keywords: Lanthanides; Aminidates; Europium; Neodymium; Praseodymium; Samarium

Lanthanoid(III)-amidinate mit sechs- und siebenfach koordinierten Metallatomen

Inhaltsübersicht. Die kristallinen Lithium *N,N′*-diorganoamidinate Li[PhC(NR)$_2$] (**1**: R = *c*-C_6H_{11}, **2**: R = *i*Pr) und Li[$(CF_3)_3C_6H_2C$-(N-*c*-$C_6H_{11})_2$] (**3**) wurden durch Reaktion von Phenyllithium bzw. 2,4,6-Tris(trifluormethyl)phenyllithium mit den Diorganocarbodiimiden R-N=C=N-R (R = *c*-C_6H_{11}, *i*Pr) erhalten. Diese Amidinate wurden zur Synthese der homoleptischen Lanthanoid(III)amidinate [PhC(N-*c*-$C_6H_{11})_2]_3$Ln (**4−6**: Ln = Pr, Nd, Sm) und [PhC(N*i*Pr)$_2]_3$Pr (**7**) verwendet. Siebenfach koordinierte Lewis-Basenaddukte des Typs [PhC($NSiMe_3)_2]_3$Ln(NCPh) (**8,9**: Ln = Sm, Eu) wurden durch Addition von Benzonitril an die homoleptischen Vorstufen [PhC($NSiMe_3)_2]_3$Ln dargestellt. Die Verbindungen **2** (als THF-Addukt), **4**, **6**, **8** und **9** wurden durch Einkristall-Röntgenstrukturanalysen strukturell charakterisiert.

Introduction

The discovery of *Brookhart* et al. that late transition metal complexes containing diimine ligands can catalyze ethylene polymerization while suppressing *β*-hydride elimination has enormously stimulated the use of chelating nitrogen-containing ancillary ligands in main group, transition metal and *f*-element chemistry [1, 2]. Typical examples of such ligands besides diimines include amidinates [3−8], guanidinates [9, 10] and *β*-diketiminates [11−17]. For the lanthanide elements, several homoleptic [18, 19] and heteroleptic [20−26] amidinates, guanidinates [27] and *β*-diketiminates [28] have been reported. Most recently, it has been discovered, that homoleptic lanthanide amidinates and their THF adducts exhibit extremely high activity for the ring-opening polymerization of *ε*-caprolactone at room temperature [29]. As part of our ongoing studies in this field, we report here the preparation and structural characterization of several crystalline lithium diorganoamidinates and their use as precursors for the synthesis of homoleptic lanthanide(III) amidinates with six-coordinate metal atoms. In addition, novel seven-coordinate benzonitrile adducts of the type [PhC($NSiMe_3)_2]_3$Ln(NCPh) are described.

Results and Discussion

Syntheses and spectroscopic data

The synthesis of lithium-N,N′-bis(trimethylsilyl)benzamidinate, Li[PhC($NSiMe_3)_2$], from benzonitrile and LiN($SiMe_3)_2$ has been reported as early as 1973 by Sanger et al. [30]. Subsequently several p-substituted derivatives have become available as pure crystalline solids by adopting the same synthetic route [31]. In contrast, 2,4,6-trisubstituted anions of the type [$R_3C_6H_2C(NSiMe_3)_2]^-$ were prepared by reacting either mesityllithium or 2,4,6-tris(trifluoromethyl)-phenyllithium with N,N′-bis(trimethylsilyl)carbodiimide. N-Alkylated lithium benzamidinates are also accessible via metallation of the NH functional group in benzamidines [32−34] or addition of lithium amides to benzonitrile [32]. We chose the carbodiimide route to make several lithium benzamidinates readily available in large amounts and in

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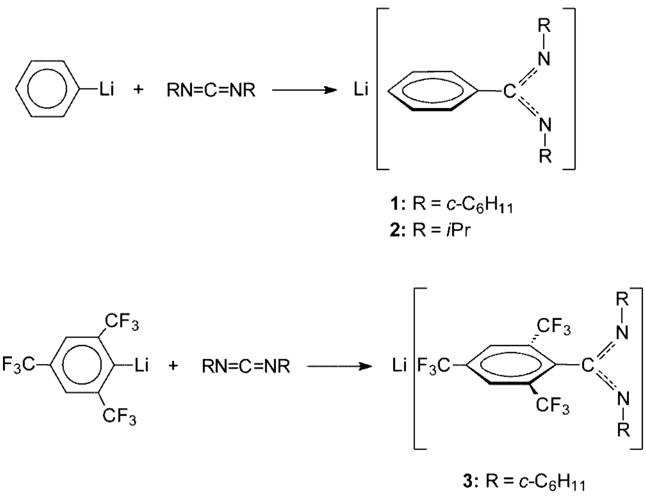
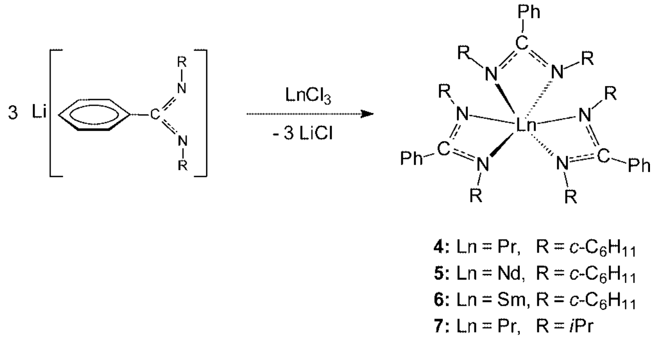
the form of pure, crystalline materials. The reagents dicyclohexylcarbodiimide (DCC) and diisopropylcarbodiimide are both commercially available because of their wide application in peptide syntheses. Scheme 1 depicts the preparation of the lithium salts **1−3**:



Scheme 1 Preparation of lithiumamidinates **1−3**.

All three reactions can be carried out on a large scale and afford the pure unsolvated lithium salts **1−3** as well-defined, crystalline solids. While the yields are moderate in the case of **1** and **2**, the low yield of **3** is due to severe losses of material during the necessary recrystallization from *n*-hexane. An analogous reaction of 2,4,6-tris(trifluoromethyl)-phenyllithium with diisopropylcarbodiimide in diethylether failed to produce a crystalline reaction product. All three lithium salts are highly moisture-sensitive and freely soluble in diethylether, THF and toluene. Solubility in *n*-hexane is poor for **1** and **2**, but quite high in the case of **3**. Characteristic IR bands of medium intensity at *ca.* 1637, 1596 and 1635 cm^{-1} can be attributed to the antisymmetric valence vibrations of the NCN units in the benzamidinate anions. A strong band at 1151 cm^{-1} in the spectrum of **3** is caused by the C−F stretching vibration. The EI mass spectrum of **2** gave an indication of a dimeric solid state structure in the unsolvated lithium benzamidinates. The peak at *m*/*z* 420 corresponds to the dimeric unit $[\{C_6H_5C(NC_3H_7)_2\}Li]_2$. A fragment at *m*/*z* 377 results from abstraction of an isopropyl group from this dimer. The dimeric structure is in fact a common feature in this class of compounds [35] and was later verified by the crystal structure determination of the THF adduct of **2** (*vide infra*).

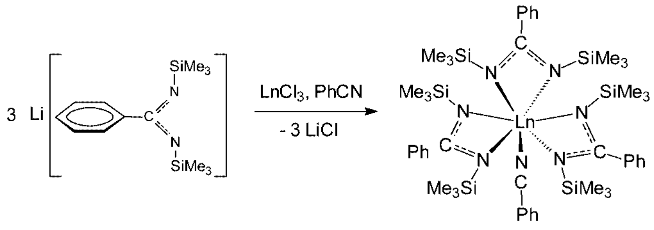
The lithium benzamidinate precursors **1−3** have subsequently been used to prepare a series of homoleptic lanthanide(III) benzamidinates. Such compounds containing *N-silylated* benzamidinate ligands have been reported several years ago [18], while related species with three N-alkylated amidinate have only recently been described by *Shen* et al. [29]. The compounds **4−7** were prepared according to Scheme 2:



Scheme 2 Preparation of the homoleptic lanthanide(III) amidinates **4−7**.

The products were isolated by crystallization from *n*-hexane. All four lanthanide(III) benzamidinates are highly moisture-sensitive, but can be briefly handled in dry air. The two praseodymium derivatives are light green, while the Nd complex **5** forms light blue crystals and the samarium compound **6** is dark blue. They are all freely soluble in diethylether, toluene and *n*-hexane. It should be noted that a bis-THF adduct of **5** has recently been reported by *Shen* et al. [29]. Mass spectra of **4−6** show the molecular ions of the homoleptic lanthanide(III) benzamidinate molecules. ^{1}H NMR spectra could be obtained in all four cases. They exhibit the typical paramagnetic shift of the signals due to the fact that the lanthanide ions act as "intramolecular shift reagents". For example, the signals of the phenyl protons in the spectra of **4**, **6** and **7** are shifted to higher field and appear in a range of δ 9.22−13.63. Notable in all spectra is the pronounced separation of the peaks corresponding to the *ortho*-, *meta*- and *para*-phenyl protons as well as the *tertiary* cyclohexyl protons.

As mentioned above, several homoleptic lanthanide(III) amidinate complexes have been isolated in the form of their THF adducts. Typical examples include the compounds $[PhC(N\text{-}c\text{-}C_6H_{11})_2]_3Ln(THF)_2$ (Ln = Y, Nd, Yb) [29]. However, none of these adducts involving coordination numbers higher than 6 have been structurally characterized until now. We found, that 1:1 adducts are also readily formed with nitriles such as acetonitrile or benzonitrile. Due to the presence of six trimethylsilyl substituents, lanthanide benzamidinates of the type $[PhC(NSiMe_3)_2]_3Ln$ [18, 19] are highly soluble in non-polar organic solvents such as toluene or even *n*-pentane and *n*-hexane. Somewhat surprisingly, the solubility in MeCN was found to be much lower. Thus acetonitrile is the most suitable solvents for recrystallization of these complexes. Obviously, this remarkable difference in solubility is associated with adduct formation in the presence of acetonitrile. However, thus far no well-defined MeCN adducts could be isolated, because the coordinated acetonitrile is easily lost upon drying of the adducts. In order to obtain crystalline nitrile adducts we investigated the reaction of $[PhC(NSiMe_3)_2]_3Ln$ complexes with benzonitrile. In this case it is not necessary to isolate the homoleptic lanthanide(III) benamidinates. 1:1 adducts with PhCN are easily accessible directly by reacting anhydrous lanthanide trichlorides with three equivalents of $Li[PhC(NSiMe_3)_2]$ in the presence of one equivalent of PhCN according to Scheme 3:



8: Ln = Sm, **9**: Ln = Eu

Scheme 3 Preparation of the benzonitrile adducts **8** and **9**.

When this reaction is carried out in *n*-hexane, the products can be crystallized directly from the filtered reaction mixtures. The samarium derivative **8** forms colorless crystals, while the Eu complex **9** is bright yellow. The IR spectra of **8** and **9** are almost superimposable and confirm the proposed composition. For example, in the spectrum of **2** the monosubstituted phenyl rings give rise to four overtone and combination bands in the range of 1945−1783 cm^{-1}, ring valence vibrations at 1600 and 1578 cm^{-1}, the four CH rocking vibrations at 1177, 1165, 1073 and 1028 cm^{-1}, as well as the CH wagging vibration at 756 cm^{-1} and the inplane ring deformation band at 682 cm^{-1} [36]. The band at 2249 cm^{-1} can be attributed to the coordinated nitrile group. The $SiMe_3$ groups absorb at 2959 (ν_{as} CH_3), 2898 (ν_s CH_3), 1430 (δ_{as} CH_3), 1246 (δ_s CH_3), 834 (CH_3 rocking), 700 (ν_{as} SiC_3) [37], and 635 cm^{-1} (ν_s SiC_3, intensive Raman emission). Bands at 1663, 1490, and 1395 cm^{-1} can be attributed to the chelating NCN units. The Raman spectrum of **2** exhibits no emission at 1663 am^{-1} but an intensive line at 1408 cm^{-1}. EI mass spectra indicate a relatively weak bonding of the benzonitrile ligand as they show only the parent $[PhC(NSiMe_3)]_3Ln]^+$ ions as the highest peaks. ^1H NMR data and elemental analyses confirm the composition of the two compounds.

The results described here once again demonstrate that especially in *f*-element chemistry almost any cyclopentadienyl complex can be duplicated by replacing Cp or Cp* with bulky heteroallylic ligands as “steric cyclopentadienyl equivalents” [4]. Although this is most important for the design of novel catalytically active species, the successful preparation of Lewis-base adducts of $[PhC(NSiMe_3)_2]_3Ln$ complexes also deserves special attention. The benzonitrile adducts **8** and **9** can be regarded as benzamidinate analogues of the well known Lewis-base adducts of the tris(cyclopentadienyl)lanthanides(III), $(C_5H_5)_3LnL$ (L = donor ligand) [38].

Crystal structures

Single crystal X-ray diffraction studies have been carried out on the compounds **2** (as its THF adduct), **4**, **6**, **8** and **9**. Figures 1−3 show the molecular structures of **2**, **6** and **9**. Crystal and structure refinement data for all five compounds are listed in Table 1. Important bond lengths and angles are listed in Table 2.

The lithium benzamidinate **2** crystallizes from THF/toluene as a dimer containing two molecules of coordinated THF. The dimer adopts a ladder-like structure which is typical for alkali metal alkoxysilylamides [39, 40] and alkali metal diiminosulfinates [41, 42] as well as the *N*-silylated

Table 1 Crystal data and details of structure determination for **2**, **4**, **6**, **8** and **9**

	2	**4**	**6**	**8**	**9**
Empirical formula	$C_{34}H_{54}Li_2N_4O_2$	$C_{63}H_{93}N_6O_{1.50}Pr$	$C_{63}H_{93}N_6O_{1.50}Sm$	$C_{49}H_{81}N_7Si_6Sm$	$C_{49}H_{81}EuN_7Si_6$
M_r / $gmol^{-1}$	564.69	1099.34	1108.78	1087.10	1088.71
Crystal habit, color	colorless blocks	light green prisms	dark blue prisms	colorless blocks	yellow blocks
Crystal system	monoclinic	rhombohedral	rhombohedral	monoclinic	monoclinic
Space group	$P2_1/c$	R-3	R-3	$P2_1/n$	$P2_1/n$
a / Å	9.4370(10)	14.722(2)	14.757(2)	15.3370(10)	15.330(3)
b / Å	17.086(3)	14.722(2)	14.757(2)	16.471(2)	16.466(2)
c / Å	11.191(2)	50.886(10)	50.961(10)	23.438(4)	23.419(4)
α / °	90	90	90	90	90
β / °	101.980(10)	90	90	92.220(10)	92.182(10)
γ / °	90	120	120	90	90
V / $Å^3$	1765.1(5)	9551(3)	9611(3)	5916.4(13)	5908(2)
Z; F(000)	2; 616	6; 3504	6; 3522	4; 2280	4; 2284
$\rho_{(calc.)}$ /gcm^{-3}	1.062	1.147	1.149	1.220	1.224
Crystal size / mm	1.00 × 0.60 × 0.50	0.40 × 0.30 × 0.20	0.50 × 0.50 × 0.50	0.50 × 0.40 × 0.40	0.50 × 0.50 × 0.20
Temperature / K	153(2)	153(2)	153(2)	153(2)	153(2)
Absorption coeff. μ / mm^{-1}	0.065	0.807	0.958	1.150	1.220
2θ range / °	3.51 − 24.98	3.02 − 22.50	3.57 − 22.49	3.60 − 22.53	3.60 − 22.54
Measured reflexes	5797	6027	4380	13455	7750
Independent reflexes, (R_{int})	3087, (0.0507)	2761, (0.0324)	2791, (0.0546)	7740, (0.0422)	7726, (0.1367)
Refined parameters	194	215	215	568	568
Final R indices [I>2σ(I)] R1, wR2	0.0769, 0.1852	0.0444, 01107	0.0352, 0.0927	0.0318, 0.0699	0.0403, 0.0929
R indices (all Data) R1, wR2	0.1212, 0.2376	0.0580, 01295	0.0368, 0.0943	0.0428, 0.0777	0.0530, 0.1080
Goodness-of-fit on F^2	1.040	1.124	1.096	1.008	1.040
Largest difference peak and hole / $eÅ^{-3}$	0.450 / −0.273	1.509 / −0.781	1.431 / −0.635	0.463 / −0.415	1.031 / −1.455

Table 2 Selected bond lengths and bond angles for **2**, **4**, **6**, **8** and **9**

Bond lengths (pm) and -angles (°)	**2**	**4**	**6**	**8**	**9**
M−N	203.0(7), 217.6(7)	246.0(4)−246.8(4)	242.4(3)−243.1(3)	244.9(3)−253.9(3)	242.3(4)−252.8(4)
$N-C_{(amidinate)}$	131.9(4)−134.2(4)	132.9(7)−133.2(7)	133.0(5)−133.4(5)	133.1(5)−134.0(5)	132.6(7)−134.2(7)
$M-N_{(benzonitrile)}$	−	−	−	263.3(4)	261.3(5)
$C-N_{(benzonitrile)}$	−	−	−	115.3(3)	114.6(7)
$N-C-N_{(amidinate)}$	117.2(2)	117.0(5)	116.7(3)	118.7(3)−119.3(3)	118.6(5)
N−M−N	121.7(3)	54.8(2)	55.69(10)	54.91(10)−55.08(10)	55.04(14)−55.33(14)

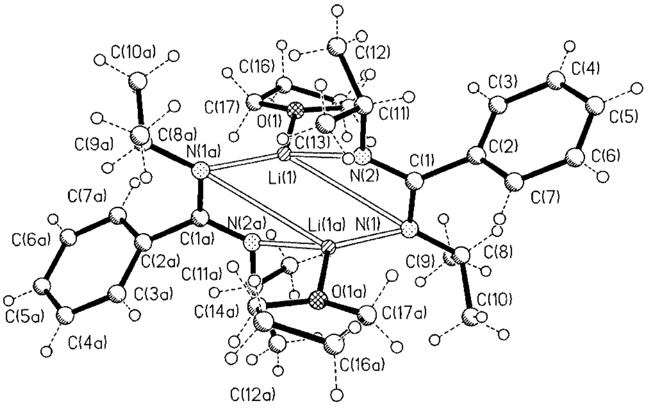


Figure 1 Molecular structure of **2** in the crystal.

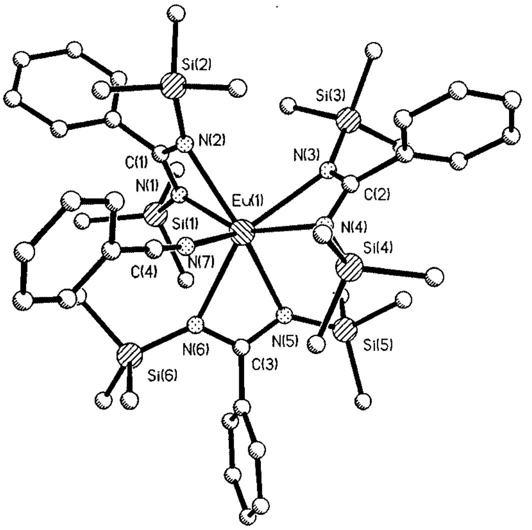


Figure 3 Molecular structure of **9** in the crystal.

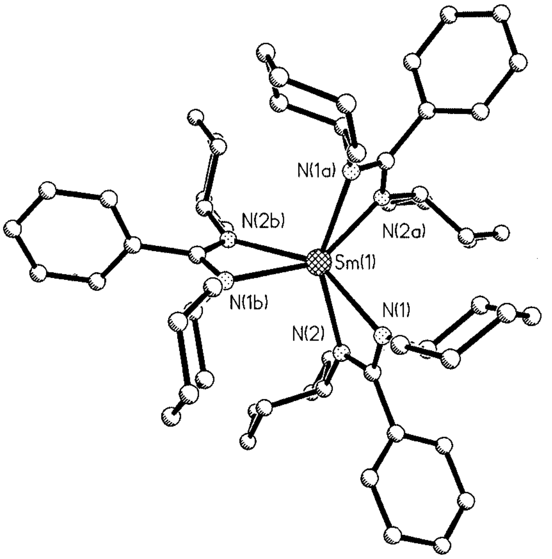


Figure 2 Molecular structure of **6** in the crystal.

lithium benzamidinate $[\{MeC_6H_4C(NSiMe_3)_2\}Li(THF)]_2$ [35]. In the central unit two four-membered CN_2Li rings enclose angles of 99.1° with the central four-membered Li_2N_2 ring system. The central Li_2N_2 ring is planar, in contrast to the structure of $[\{MeC_6H_4C(NSiMe_3)_2\}Li(THF)]_2$ where the Li_2N_2 ring is folded by 26.3° along the Li−Li axis. This structural difference can be traced back to the lower steric demand of the isopropyl groups as compared to the bulkier trimethylsilyl groups. Each lithium ion is coordinated in a distorted tetrahedral fashion by two N atoms of one NCN chelating unit, one nitrogen of an opposite benzamidinate ligand and one THF oxygen. The Li−N distances are in the range of 203.0−217.6 pm and are thus in good agreement with those typical for four-coordinate lithium (204−211 pm) [43]. A characteristic structural feature of all *N*-silylated metal benzamidinates is the large torsion angle between the phenyl ring and the NCN chelating unit, which in the case of **2** is 77°.

X-ray quality crystals of **5** and **6** were grown by slow cooling of hot saturated solutions in THF/*n*-hexane mixtures to room temperature. As the two compounds are isostructural, only the molecular structure of the samarium derivative **6** is depicted in Figure 2. The central Sm atom is coordinated be three chelating benzamidinate ligands in a distorted octahedral fashion. The three four-membered SmNCN rings are planar within 7 pm and are twisted by 77.2° with respect to each other. This arrangement minimizes steric repulsion between opposite cyclohexyl rings. The average Sm−N bond length is 242.8 pm. With 79.4° the torsion angle torsion angle between the phenyl ring and the NCN chelating unit is even larger than in **2**. This precludes any electronic conjugation between the two π-systems.

The two benzonitrile adducts **8** and **9** have also been structurally characterized by X-ray diffraction. As both compounds are isostructural, only the molecular structure of the Eu derivative is shown in Figure 3. Lewis-base adducts of homoleptic lanthanide tris[N,N′-bis(trimethylsilyl)-benzamidinates] are formally seven-coordinate, highly crowded molecules, in which the central lanthanide ion is bonded only to nitrogen atoms. Considered the high steric demand of the heteroallylic ligand (intermediate between Cp and Cp*) it is evident that only "slim" ligands such as nitriles or isonitriles can successfully enter the coordination sphere of the lanthanide metal to form stable 1:1 adducts. The four-membered LnNCN chelate rings are essentially planar. In both compounds **8** and **9** the average N−Ln−N angle is 55°. The average Ln−N bond lengths are 248.7 pm (**1**) and 247.2 pm (**2**), respectively. These values can be favorably compared with those found in other crystallographically characterized lanthanide benzamidinates [18−20, 22, 23]. As indicated by the mass spectrometric investigation the bonding of the benzonitrile ligand is fairly weak (**1**: Sm−N 261.3, **2**: Eu−N 261.3 pm). This reflects the severe steric crowding in these molecules.

Experimental

General Comments. The reactions were carried out in an inert atmosphere of dry nitrogen using standard dry box and Schlenk techniques. IR spectra were recorded on a Bio-Rad FTS 7 spectrometer. NMR spectra were recorded on a Bruker AM 400 NMR spectrometer. Elemental analyses were performed at the Department of Inorganic Chemistry of the University of Göttingen. Melting and decomposition points were determined on a Büchi 510 apparatus. The starting materials $LnCl_3$ (anhydrous) [44], $Li[PhC(NSiMe_3)_2]$ [30, 31] and $(CF_3)_3C_6H_2Li$ [45, 46] and were synthesized according to the literature procedures. The compounds R-N=C=N-R (R = c-C_6H_{11}, *i*Pr) and phenyllithium were purchased from Aldrich and used as received.

Lithium-N,N′-dicyclohexylbenzamidinate, Li[PhC(N-c-C_6H_{11})$_2$] (**1**)

Phenyllithium (84.05 g, 1 mol), dissolved in 550 ml of a diethylether/cyclohexane mixture (7/3), was added to a solution of *N,N′*-dicyclohexylcarbodiimide (206.33 g, 1 mol) in diethylether (700 ml). Stirring at room temperature was continued for 12 h, whereby the product partially precipitated. The solvent mixture was distilled off under reduced pressure, and the crude product was recrystallized from diethylether/toluene (2:1). After cooling to 0 °C for 12 the crystals were separated by filtration, washed with *n*-hexane (250 ml) and dried *in vacuo* (12 h) to give 123.77 g (44 %) of unsolvated **1** as a colorless, crystalline solid, which melts at 108 °C under decomposition.
Analyses: Calcd.: C 78.6, H 9.4, N 9.7 % for $C_{29}H_{27}LiN_2$ (290.38) (found: C 77.4, H 8.9, N 9.3 %).

^{1}H NMR (25 °C, C_6D_6): δ 7.27 (m, 5H, $C_6\mathit{H}_5$), 3.11 (m, 1H, $C\mathit{H}C_5H_{10}$), 2.95 (m, 1H, $C\mathit{H}C_5H_{10}$), 0.92−2.28 (m, 20H, $CHC_5\mathit{H}_{10}$). **^{7}Li NMR** (25 °C, C_6D_6): δ 1.75. **^{13}C NMR** (25 °C, THF-d_8): δ 171.4 [$C_6H_5\mathit{C}(NC_6H_{11})_2$]; 142.8 ($C_6H_5$, C_{ipso}); 131.1, 129.7, 128.9, 127.9, 126.9 (C_6H_5); 59.6 ($\mathit{C}HC_5H_{10}$); 39.1, 27.1, 26.7 ($CH\mathit{C}_5H_{10}$). **MS** (EI, 70 eV): *m/z* 284 (M−Li, 14 %), 201 [$C_6H_5CNH(NC_6H_{11})$, 14 %], 121 [$C_6H_5C(NH_2)_2$, 14 %], 104 (C_6H_5CNH, 20 %], 83 (C_6H_{11}, 54 %), 55 (C_4H_7, 100 %). **IR** (KBr) cm^{-1}: 3060(m), 2114(vs), 1637(m), 1344(s), 1144(m), 1071(s), 985(m), 946(w), 919(w), 888(m), 838(w), 778(s), 706(s), 660(w), 641(w).

Lithium-N,N′-diisopropylbenzamidinate, Li[PhC(NiPr)$_2$] (**2**)

In a similar manner, phenyllithium (30.26 g, 0.36 mol), dissolved in 200 ml of a diethylether/cyclohexane mixture (7/3), was slowly added to a solution of *N,N′*-diisopropylcarbodiimide (45.43 g, 0.36 mol) in diethylether (300 ml). Stirring at room temperature was continued for 12 h, the reaction mixture was concentrated to a total volume of 150 ml, diluted with toluene (80 ml) and cooled to 0 °C for 24 h. The resulting crystals were isolated by filtration, washed with *n*-hexane (150 ml) and dried *in vacuo* (12 h) to give 62.78 g (83 %) **2** in the form of colorless, moisture-sensitive crystals. M.p. 108 °C.
Analyses: Calcd.: C 74.3, H 9.1, N 13.3 % for $C_{13}H_{19}LiN_2$ (210.25) (found: C 73.8, H 8.9, N 12.8 %).

^{1}H NMR (25 °C, THF-d_8): δ 7.30 (m, 2H, $C_6\mathit{H}_5$), 7.21 (m, 1H, $C_6\mathit{H}_5$), 7.07 (m, 3H, $C_6\mathit{H}_5$), 3.00 [sept, 2H, $C\mathit{H}(CH_3)_2$, ^{3}J = 6.2 Hz], 0.95 [d, 12H, $CH(C\mathit{H}_3)_2$, ^{3}J = 6.2 Hz]. **^{7}Li NMR** (25 °C, C_6D_6): δ 1.64. **^{13}C NMR** (25 °C, THF-d_8): δ 174.1 [$C_6H_5\mathit{C}(NC_3H_7)_2$]; 141.5 ($C_6H_5$, C_{ipso}); 129.0, 128.4, 127.8, 127.7, 126.7 (C_6H_5); 48.4 [$\mathit{C}H(CH_3)_2$]; 27.3 [$CH(\mathit{C}H_3)_2$]. **MS** (EI, 70 eV): *m/z* 420 [$\{[C_6H_5C(NC_3H_7)_2Li\}_2$ = M, 20 %], 377 [M−C_3H_7, 10 %], 217 [$\{C_6H_5C(NC_3H_7)_2\}Li_2$, 94 %], 203 [$C_6H_5C(NC_3H_7)_2$, 20 %], 132 [$C_6H_5C(NC_2H_5)_2$, 15 %], 104 ($C_6H_5CNH$, 10 %), 77 ($C_6H_5$, 18 %), 58 ($HNC_3H_7$, 44 %). **IR** (KBr) cm^{-1}: 3058(s), 2615(m), 156(m), 1410(vs), 1342(vs), 1167(s), 1127(s), 1073(m), 1043(m), 996(m), 941(w), 911(w), 821(w), 783(s), 734(m), 703(vs), 675(m), 625(w), 511(m), 488(m), 438(m).

Lithium-N,N′-dicyclohexyl-2,4,6-tris(trifluoromethyl)benzamidinate, Li[(CF_3)$_3C_6H_2C$(N-c-C_6H_{11})$_2$] (**3**)

A solution of *n*-butyllithium (6.81 g, 106.3 mmol) in *n*-hexane (98.4 ml) was added dropwise to a solution of 1,3,5-tris(trifluoromethyl)benzene (30.00 g, 106.3 mmol) in diethylether (200 ml) at such a rate that the ether kept gently refluxing. After stirring at room temperature the mixture was transferred into a dropping funnel and added slowly to a solution of *N,N′*-dicyclohexylcarbodiimide (21.94 g, 106.3 mmol) in diethylether (200 ml). Stirring at room temperature was continued for 24 h. Evaporation of the solvent mixture under reduced pressure left a red, oily residue, which was recrystallized from boiling *n*-hexane to afford 5.53 g (11 %) **3** in the form of yellow-orange crystals. M.p. 115 °C (dec.).
Analyses: Calcd.: C 53.5, H 4.9, N 5.7 % for $C_{22}H_{24}F_9LiN_2$ (494.37) (found: C 51.3, H 4.3, N 5.3 %).

^{1}H NMR (25 °C, THF-d_8): δ 8.20 [s, 2H, $C_6\mathit{H}_2(CF_3)_3$], 2.20 (m, 2H, $C\mathit{H}C_5H_{10}$), 0.85−1.80 (m, 20H, $CHC_5\mathit{H}_{10}$). **^{19}F NMR** (25 °C, THF-d_8): δ −57.0 (s, 6F, *o*-CF_3), −62.7 (s, 3F, *p*-CF_3). **MS** (EI, 70 eV): *m/z* 488 [$(CF_3)_3C_6H_2C(NC_6H_{11})_2H$, 5 %], 419 [$(CF_3)_2C_6H_2C(NC_6H_{11})_2$, 84 %], 325 [$(CF_3)_3C_6H_2C(NH_2)_2$, 87 %], 104 ($C_6H_5CNH$, 100 %), 83 ($C_6H_{11}$, 36 %). **IR** (KBr) cm^{-1}: 1653(m), 1522(m), 1369(m), 1303(m), 1281(s), 1202(s), 1151(s), 1109(m), 1057(m), 1029(m), 985(w), 915(m), 890(w), 845(w), 806(m), 685(m), 660(w), 602(w), 560(w), 429(w).

Preparation of the homoleptic lanthanide(III)amidinates **4−7** *(General Procedure)*

A solution of the lithium amidinate in THF (100 ml) was added dropwise to a suspension of the given amount of anhydrous lanthanide trichloride in THF (80 ml), and the mixture was stirred at room temperature for 12 h. After evaporation to dryness, the residue was extracted with boiling *n*-hexane (3 x 100 ml). Concentration of the combined extracts to a total volume of *ca.* 100 ml and cooling to −20 °C afforded the crystalline product, which was isolation by filtration and drying.

Tris(N,N′-dicyclohexylbenzamidinato)praseodymium(III) (**4**)

From 3.00 g (12.1 mmol) $PrCl_3$ and 10.64 g (36.4 mmol) **1** 4.63 g (39 %) light green crystals of **4** were isolated. M.p. 195 °C.
Analyses: Calcd.: C 69.9, H 8.2, N 8.5 % for $C_{57}H_{81}N_6Pr$ (991.23) (found: C 68.8, H 7.9, N 8.2 %).

^{1}H NMR (25 °C, C_6D_6): δ 10.11 (m, 9H, $C_6\mathit{H}_5$), 9.23 (m, 6H, $C_6\mathit{H}_5$), 2.83 (m, 2H, $C\mathit{H}C_5H_{10}$), 1.90 (m, 2H, $C\mathit{H}C_5H_{10}$), 1.78 (m, 2H, $C\mathit{H}C_5H_{10}$), 0.82−1.70 (m, 60H, $CHC_5\mathit{H}_{10}$). **MS** (EI, 70 eV): *m/z* 991 (M, 26 %), 908 ($M-C_6H_{11}$, 26 %), 708 [$M-C_6H_5C(NC_6H_{11})_2$, 100 %], 283 [$C_6H_5C(NC_6H_{11})_2$, 100 %], 201 [$C_6H_5CNH(NC_6H_{11})$, 84 %], 121 [$C_6H_5C(NH_2)_2$, 63 %], 104 (C_6H_5CNH, 100 %), 98 (HNC_6H_{11}, 46 %). **IR** (KBr) cm^{-1}: 3437(w), 3059(m), 2668(m), 1642(m), 1577(m), 1345(vs), 1312(s), 1244(m), 1201(s), 1153(m), 1071(s), 1026(m), 967(s), 914(m), 889(m), 842(w), 775(s), 754(m), 701(vs), 661(m), 500(w), 483(1), 424(m), 364(m), 322(vs).

Tris(N,N′-dicyclohexylbenzamidinato)neodymium(III) (**5**)

3.00 g (12.0 mmol) $NdCl_3$ and 10.50 g (36.2 mmol) **1** gave 4.49 g (40 %) light blue crystals of **5**. M.p. 163 °C.
Analyses: Calcd.: C 68.8, H 8.2, N 8.5 % for $C_{57}H_{81}N_6Nd$ (994.56) (found: C 68.2, H 7.8, N 8.3 %).

^{1}H NMR (25 °C, C_6D_6): δ 7.05−7.45 (m, 15H, $C_6\mathit{H}_5$), 3.85 (m, 2H, $C\mathit{H}C_5H_{10}$), 2.85 (m, 2H, $C\mathit{H}C_5H_{10}$), 2.65 (m, 2H, $C\mathit{H}C_5H_{10}$), 0.85−2.15 (m, 60H, $CHC_5\mathit{H}_{10}$). **MS** (EI, 70 eV): *m/z* 994 (M, 25 %), 911 ($M-C_6H_{11}$, 17 %), 711 [$M-C_6H_5C(NC_6H_{11})_2$, 100 %], 283 [$C_6H_5C(NC_6H_{11})_2$, 100 %], 201 [$C_6H_5CNH(NC_6H_{11})$, 87 %], 121 [$C_6H_5C(NH_2)_2$, 65 %], 104 (C_6H_5CNH, 100 %), 98 (HNC_6H_{11}, 48 %). **IR** (KBr) cm^{-1}: 3436(w), 3080(m), 1641(s), 1601(w), 1345 (vs), 1312(s), 1200(m), 1152(m), 1071(m), 1027(m), 987(m), 914(w), 888(w), 776(m), 701(vs), 661(w), 544(w), 484(w), 423(w).

Tris(N,N′-dicyclohexylbenzamidinato)samarium(III) (**6**)

The reaction of 3.00 g (11.7 mmol) $SmCl_3$ and 10.25 g (35.3 mmol) **1** afforded 1.62 g (14 %) dark blue crystals of **6**. M.p. 208 °C.
Analyses: Calcd.: C 68.4, H 8.2, N 8.4 % for $C_{57}H_{81}N_6Sm$ (1000.68) (found: C 68.6, H 7.9, N 7.8 %).

^{1}H NMR (25 °C, C_6D_6): δ 9.42 (d, 6H, *o*-$C_6\mathit{H}_5$), 8.21 (t, 6H, *m*-$C_6\mathit{H}_5$), 8.02 (t, 3H, *p*-$C_6\mathit{H}_5$), 1.97 (m, 6H, $C\mathit{H}C_5H_{10}$), 0.82−1.91 (m, 60H, $CHC_5\mathit{H}_{10}$). **MS** (EI, 70 eV): *m/z* 1001 (M, 3 %), 718 [$M-C_6H_5C(NC_6H_{11})_2$, 50 %], 434 [$C_6H_5C(NC_6H_{11})_2Sm$, 9 %], 283 [$C_6H_5C(NC_6H_{11})_2$, 100 %], 201 [$C_6H_5CNH(NC_6H_{11})$, 79 %], 121 [$C_6H_5C(NH_2)_2$, 51 %], 104 (C_6H_5CNH, 85 %). **IR** (KBr) cm^{-1}: 3437(w), 3060(m), 2667(m), 2120(m), 1641(m), 1577(m), 1544(s), 1362(vs), 1345(vs), 1311(s), 1245(m), 1204(s), 1163(m), 1153(s), 1071(s), 1026(m), 987(s), 914(s), 889(s), 842(m), 775(vs), 755(m), 701(vs), 662(vs), 516(m), 500(m), 483(m), 424(s), 366(s).

Tris(N,N′-diisopropylbenzamidinato)praseodymium(III) (**7**)

Treatment of 1.30 g (6.1 mmol) $PrCl_3$ with 3.83 g (18.2 mmol) **2** gave 0.55 g (14 %) **7** as light green crystals. M.p. 125 °C.
Analyses: Calcd.: C 62.4, H 7.7, N 11.2 % for $C_{39}H_{57}N_6Pr$ (750.84) (found: C 61.5, H 7.5, N 10.8 %).

^{1}H NMR (25 °C, C_6D_6): δ 13.63 (d, 6H, *o*-$C_6\mathit{H}_5$), 9.98 (t, 6H, *m*-$C_6\mathit{H}_5$), 9.22 (t, 3H, *p*-$C_6\mathit{H}_5$), −0.38 [m, 6H, $C\mathit{H}(CH_3)_2$], −3.98 [m, 36H, $CH(C\mathit{H}_3)_2$]. **MS** (EI, 70 eV): *m/z* 750 (M, 6 %), 707 ($M-C_3H_7$, 10 %), 547 [$M-C_6H_5C(NC_3H_7)_2$, 29 %], 203 [$C_6H_5C(NC_3H_7)_2$, 27 %], 132 [$C_6H_5C(NC_2H_5)_2$, 38 %], 104 (C_6H_5CNH, 100 %), 58 (HNC_3H_7, 53 %). **IR** (KBr) cm^{-1}: 3060(m), 2611(m), 1642(s), 1602(m), 1577(m), 1337(vs), 1275(m), 1208(s), 1166(s), 1135(s), 1073(m), 1007(vs), 975(m), 947(m), 911(m), 844(w), 820(w), 780(s), 722(s), 702(vs), 582(w), 541(w), 503(w), 469(w).

Benzonitrile-tris[N,N′-bis(trimethylsilyl)benzamidinato]samarium(III) (**8**)

A mixture of anhydrous $SmCl_3$ (3.00 g, 11.7 mmol), Li[$PhC(NSiMe_3)_2$] (9.49 g, 35.1 mmol) and PhCN (1.21 g, 11.7 mmol) in *n*-hexane (100 ml) was stirred for 24 h at room temperature. The precipitated LiCl was removed by filtration, the clear filtrate was concentrated to a total volume of *ca.* 50 ml and cooled to −25 °C (24 h). 8.57 g (70 %) of **8** were isolated as colorless, moisture-sensitive crystals. M.p. 116 °C.
Analyses: Calcd.: C 52.9, H 7.1, N 9.4 % for $C_{46}H_{74}N_7Si_6Sm$ (1044.38) (found: C 54.0, H 7.1, N 8.4 %).

^{1}H NMR (25 °C, C_6D_6): δ 10.37 (d, 6H, *o*-$C_6\mathit{H}_5$), 8.12 (t, 6H, *m*-$C_6\mathit{H}_5$), 7.97 (m, 3H, *p*-$C_6\mathit{H}_5$), 6.87 (d, 2H, *o*-C_6H_5CN), 6.75 (m, 1H, *p*-C_6H_5CN), 6.58 (t, 2H, *m*-C_6H_5CN), −1.23 [s, 54H, $Si(CH_3)_3$]. **MS** (EI, 70 eV): *m/z* 943 ($M-C_6H_5CN$, 8 %), 679 [$\{C_6H_5C(NSiMe_3)_2\}_2Sm$, 100 %], 415 [$C_6H_5C(NSiMe_3)_2Sm$, 32 %], 263 [$C_6H_5C(NSiMe_3)_2$, 13 %], 176 ($C_6H_5CNSiMe_3$, 22 %), 146 [$Si_2(CH_3)_6$, 22 %], 73 [$Si(CH_3)_3$, 48 %]. **IR** (Nujol/KBr) cm^{-1}: 3062(w), 2249(w), 1664(w), 1246(vs), 1073(w), 1027(w), 977(vs), 918(m), 829(vs), 755(s), 683(s), 603(m), 554(m), 471(s), 310(s).

Benzonitrile-tris[N,N′-bis(trimethylsilyl)benzamidinato]europium(III) (**9**)

Similar to the preparation of **8**, the europium complex **9** was made from $EuCl_3$ (1.50 g, 8.8 mmol), Li[$PhC(NSiMe_3)_2$] (4.71 g, 17.4 mmol) and PhCN (0.60 g, 5.8 mmol). 2.89 g (48 %) of **9** were isolated as large, bright yellow crystals.
Analyses: Calcd.: C 52.8, H 7.1, N 9.4 % for $C_{46}H_{74}EuN_7Si_6$ (1045.38) (found: C 53.6, H 7.4, N 8.8 %).

MS (EI, 70 eV): *m/z* 944 ($M-C_6H_5CN$, 8 %), 680 [$\{C_6H_5C(NSiMe_3)_2\}_2Eu$, 100 %], 416 [$C_6H_5C(NSiMe_3)_2Eu$, 36 %], 263 [$C_6H_5C(NSiMe_3)_2$, 23 %], 176 ($C_6H_5CNSiMe_3$, 18 %), 146 [$Si_2(CH_3)_6$, 28 %], 73 [$Si(CH_3)_3$, 53 %]. **IR** (Nujol/KBr) cm^{-1}: 3421(w), 3080(w), 3062(w), 3032(w), 3022(w), 2959(m), 2898(m), 2249(m), 1945(w), 1896(w), 1809(w), 1763(w), 1663(s), 1600(w), 1578(w), 1490(m), 1456(s), 1430(s), 1395(vs), 1291(w), 1246(vs), 1177(w), 1165(w), 1144(w), 1095(w), 1073(w), 1028(w), 1001(m), 978(s), 934(m), 918(m), 870(vs), 834(vs), 783(s), 756(vs), 724(s), 699(s), 682(s), 634(w), 616(w), 603(w), 554(w), 515(w), 472(s), 434(w).

Crystal structure determination [47]

Suitable single crystals of the THF adduct of **2** were grown by sequential recrystallization of **2** from THF and toluene. Well-formed single crystals of **4** and **6** were obtained upon slow cooling of hot saturated solutions of the compounds in *n*-hexane/THF mixtures to room temperature. Single crystals of **8** and **9** were grown by slow cooling of saturated hexane solutions to −25 °C.
All crystals were measured on a Stoe-Siemens-AED four-circle diffractometer with graphite-monochromated X-radiation (Mo-K_α, $\lambda = 0.71073$ Å). The structures were solved by direct methods [47] and refined by full-matrix least-squares methods, with all non-hydrogen atoms anisotropic. The hydrogen atoms were located by difference Fourier synthesis and refined using a riding model. In the structure determinations, a weighting scheme with $w^{-1} = \sigma^2(F) + 3F^2$ was used.

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Supporting Information. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany) (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting number CSD-59285.

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