DOI: 10.1002/ejic.200800050

Donor and *ate*-Coordination in Rare-Earth Metal Bis(dimethylsilyl)amide Complexes

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Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Keywords: Rare-earth metals / Neodymium / Scandium / Silylamide

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Complete thf donor exchange is observed when complexes Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (Ln = La, Nd) are treated with the monofunctional donor molecules triphenylphosphane oxide, *N*-methylimidazole, and 1,3-dimethylimidazolin-2-ylidene. The resulting complexes Ln[N(SiHMe$_2$)$_2$]$_3$(donor)$_2$ exhibit a trigonal-bipyramidal coordination geometry with the donor molecules located in the apical positions. Bifunctional chelating donors 1,10-phenanthroline, 1,2-bis(dimethylphosphanyl)ethane, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine give discrete complexes Ln[N(SiHMe$_2$)$_2$]$_3$(phen) (Ln = Sc, La, Nd), Nd[N(SiHMe$_2$)$_2$]$_3$(dmpe), and La[N(SiHMe$_2$)$_2$]$_3$(tmeda). The phen adducts are isostructural as demonstrated for the large Nd^{3+} and small Sc^{3+} centers by X-ray structure analyses and display a distorted square-pyramidal coordination geometry in the solid state. The distinct coordination of various donor molecules implies subtle changes of the Si–H bonding which can be straightforwardly examined by NMR and FTIR spectroscopy. Ate complex {Y[N(SiHMe$_2$)$_2$]$_4$Li}$_2$ can be isolated and crystallized from Y(OTf)$_3$–Li[N(SiHMe$_2$)$_2$]–hexane reaction mixtures. Dimerization is accomplished by unusual intermolecular Li···H–Si interactions.

Introduction

Bis(dimethylsilyl)amide complexes of the rare-earth elements, Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_x$ (x = 1, Ln = Sc; x = 2, Ln = Y, La, Ce–Lu), emerged as versatile synthesis precursors according to the *extended silylamide route*.[1,2] Importantly, these discrete and (in aliphatic hydrocarbons) highly soluble amide derivatives have been successfully exploited for (pre)catalyst design.[3] Additional donor (thf) coordination is necessary to sterically saturate the Ln metal center giving rise to a trigonal bipyramidal coordination geometry in Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$.[1,2] This is in contrast to homoleptic donor-free complexes Ln[N(SiMe$_3$)$_2$]$_3$ featuring the sterically more demanding N(SiMe$_3$)$_2$ ligands.[1,4–6] Unsurprisingly, the coordinated thf in Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_x$ results from a salt metathesis synthesis protocol. Briefly, La[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ can be efficiently synthesized from LaCl$_3$(thf)$_{1.3}$ and 2.9 equiv. of LiN(SiHMe$_2$)$_2$ in thf (very pure, ate complex-free, high yield), while the thf-richer derivatives LnCl$_3$(THF)$_x$ ($x > 2$) of the smaller rare-earth elements enable the synthesis of the silylamide complexes in hexane.[2] It is assumed that thf dissociation is the initiating step in protonolytic silylamide ligand exchange as well as catalytic reactions.[3] Therefore, it can be anticipated that the reactivity of such silylamide complexes can be adjusted by distinct donor coordination. The Lewis acidity of the Ln^{3+} metal center can be uniquely probed by the SiH functionality of the silylamido ligand which tends to engage in M···H–Si β-agostic interactions.[3] Moreover, application of bifunctional chelating donor ligands will drastically affect the coordination geometry and hence the accessibility of the metal center. We have previously shown that the thf donor molecules in Y[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ can be stepwise exchanged by the N-heterocyclic carbene (nhc) 1,3-dimethylimidazolin-2-ylidene to yield complexes Y[N(SiHMe$_2$)$_2$]$_3$(nhc) and Y[N(SiHMe$_2$)$_2$]$_3$(nhc)$_2$, respectively.[7] Herein, we present a more comprehensive study on the interaction of various donor molecules with complexes Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_x$ featuring differently sized Ln metal centers. We also account for ate complexation in Ln-triflate-derived synthesis mixtures.

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Results and Discussion

Synthesis and Characterization of Complexes with Neutral Donor Ligands

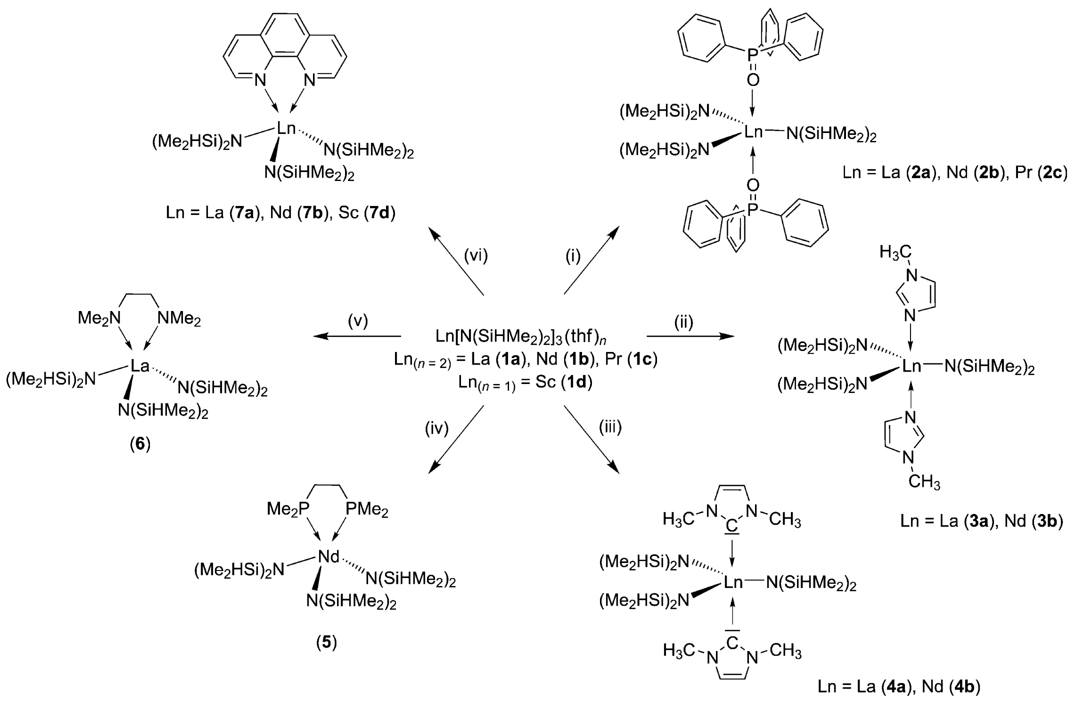
Bradley et al. have previously shown that triphenylphosphane oxide readily displaces weak Ln···Me–Si interactions in pyramidal Ln[N(SiMe$_3$)$_2$]$_3$ to form mono(adduct) La[N(SiMe$_3$)$_2$]$_3$(O=PPh$_3$).[8] Treatment of the complexes Ln[N(SiHMe$_2$)$_3$]$_3$(thf)$_2$ (**1**) with two equivalents of O=PPh$_3$ gave the bis(O=PPh$_3$) donor adducts **2a**–**c** in over 90% yield (Scheme 1). Complete thf/O=PPh$_3$ donor ligand exchange was confirmed by ^{1}H NMR spectroscopy causing a marked shift of the Si*H* proton resonances to lower field as evidenced for the diamagnetic La^{3+} derivative **2a** (e.g., δ = 5.02→5.30 ppm).[2] This trend of the Si*H* signal to appear at lower field in the presence of a stronger donor ligand could be observed for all complexes under study (see Table 1). Furthermore, the ^{31}P NMR spectrum of **2a** does not indicate any dissociation of O=PPh$_3$ as corroborated by one sharp singlet at δ = 35.1 ppm. FTIR spectroscopy offers another efficient tool to study Ln···H–Si interactions.[9–13] For complexes **2**, the peculiar Si–H stretching vibrations are characterized by pronounced low-energy shoulders in the area 1900 to 2000 cm^{-1} typical of weak agostic interactions (Table 1).[9–13] Generally, strong M···H–Si agostic interactions fall in the range 1700 to 1900 cm^{-1}.[12]

Table 1. Spectroscopic data for Ln[N(SiHMe$_2$)$_2$]$_3$(donor)$_x$.

	Donor ligand (No.)	ν(SiH) [cm^{-1}]	ν(SiH) (sh) [cm^{-1}]	^{1}H NMR δ(Si*H*) [ppm]	^{1}H NMR δ(Si*Me*) [ppm]
1a (La)[2a]	thf (2)	2051	1970	5.02	0.38
1b (Nd)[1]	thf (2)	2066	1967	–7.9	5.9
1c (Pr)[2b]	thf (2)	2060	1931	–26.2	8.43
1d (Sc)[2a]	thf (1)	2091	1920	5.03	0.37
1e (Y)[2a]	thf (2)	2072	1939	4.99	0.38
2a (La)	O=PPh$_3$ (2)	2016	1960, 1913	5.30	0.28
2b (Nd)	O=PPh$_3$ (2)	2040	2063, 2018, 1963	10.40	2.02
2c (Pr)	O=PPh$_3$ (2)	2018	1959	8.12	2.30
3a (La)	*N*-MeIm (2)	–	–	5.26	0.43
3b (Nd)	*N*-MeIm (2)	2046	–	13.00	4.02
4a (La)	nhc (2)	2062	2044	5.13	0.27
4b (Nd)	nhc (2)	2069	2039	7.62	2.57
5 (Nd)	dmpe (1)	2049	2000	1.08	4.73
6 (La)	tmeda (1)	2046	2017	5.03	0.41
7a (La)	phen (1)	2039	1923	5.23	0.34
7b (Nd)	phen (1)	2060	1939	–1.03	4.26
7d (Sc)	phen (1)	2108	2076	5.34	0.31
8 (Y)	–	2065	1948	4.78	0.48
9 (Y)[a]	–	2095	1931	4.89	0.41

[a] {Y[N(SiHMe$_2$)$_2$]$_3$}$_2$;[25] abbreviations: *N*-MeIm = *N*-methylimidazole, nhc = 1,3-dimethylimidazolin-2-ylidene, dmpe = 1,2-bis(dimethylphosphanyl)ethane, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, phen = 1,10-phenanthroline.

The exchange of thf in Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ with *N*-methylimidazole was achieved under the same reaction conditions yielding complexes Ln[N(SiHMe$_2$)$_2$]$_3$(*N*-MeIm)$_2$ (**3**) (Scheme 1). However, compared to the other bis(donor) adducts described herein, the complexes **3a** and **3b** could be obtained only in limited purity and lower yield. While the precursor compounds **1** were detected as impurities, the ^{1}H/^{13}C NMR and IR spectra confirmed complete exchange of



Scheme 1. Reaction of Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_n$ with donor molecules; (i) 2 equiv. O=PPh$_3$, toluene/hexane, 12 h at ambient temp. and 1 h at 60 °C; (ii) 2 equiv. *N*-methylimidazole, toluene/hexane, 12 h at ambient temp. and 1 h at 60 °C; (iii) 2 equiv. 1,3-dimethylimidazolin-2-ylidene, thf, ambient temp.; (iv) 1,2-bis(dimethylphosphanyl)ethane, hexane, 20 min at 60 °C and 12 h at ambient temp.; (v) tmeda, hexane, 72 h ambient temp.; (vi) 1,10-phenanthroline, toluene, 12 h at 40 °C.

both thf ligands by *N*-MeIm. As for complex **2a**, the low-field shift of the Si*H* proton resonance in **3a** (δ = 5.26 ppm) is in agreement with the presence of a stronger coordinating donor ligand. On the other hand, strong paramagnetic shifts are observed for the Nd complexes **2b** and **3b** with the Si*H* proton signals appearing at δ = 13.0 and 10.4 ppm, respectively (**1b**, δ = –7.9 ppm).[1]

Nucleophilic N-heterocyclic carbenes (nhc) such as 1,3-dimethylimidazolin-2-ylidene are also rated as strong σ-donors,[14] but display only weak π-acceptors as revealed in lanthanide adduct complexes.[15] Straightforward thf/nhc ligand exchange has been demonstrated for $Y[N(SiHMe_2)_2]_3(thf)_2$ (**1e**) suggesting a successful exchange reaction also for other Ln^{3+} centers.[7] Accordingly, addition of two equivalents of in situ-generated 1,3-dimethylimidazolin-2-ylidene[14] to a thf solution of $Ln[N(SiHMe_2)_2]_3(thf)_2$ (Ln = La, Nd) and subsequent removal of the solvent yielded complexes $Ln[N(SiHMe_2)_2]_3(nhc)_2$ as yellow (La, **4a**) and green (Nd, **4b**) powders (Scheme 1). Solutions of **4** in thf showed decomposition within several hours as indicated by a color change from green to brown (**4b**). Decomposition was also observed if solids **4** were stored at ambient temperature. Crystallization of complexes **4** from saturated hexane solutions at –35 °C was only successful after removal of insoluble decomposition products. Spectroscopic as well as microanalytical data confirmed the composition of products **4**. In contrast to **2** and **3** the signals of the SiH moieties appear less shifted (**4a**: δ = 5.13; **4b**: 7.6 ppm) suggesting an overall weaker σ-donor capability of the nhc ligand. The IR spectra revealed only high-energy shoulders of the Si–H stretching vibration [**4a**: 2062 (s), 2044 (m) (sh); **4b**: 2069 (s), 2039 (m, sh)] in agreement with the absence of any interacting SiH groups.[16]

In order to sidestep the trigonal-planar arrangement of the bis(dimethylsilyl)amido ligands as found in complexes **2**–**4** we next investigated the coordination behavior of chelating donor ligands. Stereoelectronic implications for the Ln^{3+} metal centers could be expected. 1,2-Bis(diphenylphosphanyl)ethane (diphos) and the sterically less demanding 1,2-bis(dimethylphosphanyl)ethane (dmpe) as well as the nitrogen analog tmeda (= *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) did not undergo any exchange reaction with $La[N(SiHMe_2)_2]_3(thf)_2$ (**1a**) at ambient temperature overnight. However, stirring of the reaction mixtures at elevated temperature (60 °C) or for a prolonged period of time (72 h) afforded complexes $Nd[N(SiHMe_2)_2]_3(dmpe)$ (**5**) and $La[N(SiHMe_2)_2]_3(tmeda)$ (**6**), respectively, in moderate yields (Scheme 1, Table 1). Complex **5** is a rare example of an organolanthanide(III) complex featuring a soft phosphane donor ligand.[17] Its formation seems to be driven thermodynamically by the chelate bonding of the dmpe ligand. Interestingly, the SiH spectroscopic data of lanthanum complex **6** suggest an overall weaker donor effect of tmeda compared to monodentate $O=PPh_3$ (**2a**), *N*-MeIm (**3a**) and nhc (**4a**).

In contrast, the strongly donating and rigid 1,10-phenanthroline (phen) displayed an interesting reaction. Dropwise addition of phen to $Nd[N(SiHMe_2)_2]_3(thf)_2$ (**1b**) in toluene resulted in a color change from blue to a dark purple, perambulating the entire spectral range. The observation of such intensively colored compounds is in accordance with the formation of strong charge-transfer complexes. NMR and IR spectroscopic investigations performed for the lanthanum reaction revealed an incomplete reaction after 3 h (presence of coordinated thf), prolonged stirring of the reaction mixture (12 d), however, gave complexes $Ln[N(SiHMe_2)_2]_3(phen)$ (**7a**,**b**,**d**) in high yield. Like for complexes **2a** and **3a**, the ^1H NMR spectrum of $La[N(SiHMe_2)_2]_3(phen)$ showed the SiH protons shifted considerably to lower field (δ = 5.23 ppm).[3] It is noteworthy that the scandium complex **7d** revealed the largest low-field shift of the SiH resonance (δ = 5.34 ppm). Particularly striking is the marked shift of the ring protons at C2 and C11 adjacent to the nitrogen atoms upon coordination of the phen molecule [δ = 9.06 ppm → 9.69 (**7a**), 9.94 (**7d**)]. This is in agreement with the marked charge transfer to the Lewis acidic metal center via the nitrogen atoms. FTIR spectroscopic investigation of complexes **7** revealed "agostic shoulders" of the Si–H stretching vibration for the larger metal centers La^{3+} and Nd^{3+} only (Table 1).

All bis(thf)-coordinated tris[bis(dimethylsilyl)amido] complexes of the rare-earth elements are isostructural (monoclinic space group $P2_1/c$) with the ligands adopting a distorted trigonal-bipyramidal coordination geometry.[1,2] A number of X-ray structure analyses were performed to examine the implications of donor ligand exchange for the molecular geometry in the solid-state. $Nd[N(SiHMe_2)_2]_3(O=PPh_3)_2$ (**2b**) crystallized from a toluene solution at ambient temperature in the trigonal space group $R3c$, but a severe disorder of the silylamido ligands excludes a detailed discussion of the geometrical parameters. Compared to $Nd[N(SiHMe_2)_2]_3(thf)_2$ [O–Nd–O = 163.1(1)°], complex **2b** features an undistorted trigonal-bipyramidal arrangement of the ligands with both donor ligands in the apical positions.[2] Other donor oxide bonded discrete rare-earth metal complexes include $La[N(SiMe_3)_2]_3(O=PPh_3)$,[8] $Nd(TTA)_3(O=PPh_3)_2$ [TTA = tris(theonyltrifluoroacetonate)],[18] and $Tb[N(SiMe_3)_2]_3(O=CPh_2)$.[19]

$Nd[N(SiHMe_2)_2]_3(nhc)_2$ (**4b**) crystallized from a saturated hexane solution at –35 °C in the triclinic space group $P\bar{1}$. Hence, **4b** is isostructural to the previously reported yttrium congener with the two carbene ligands located in the apical positions of a slightly distorted trigonal bipyramid [Figure 1, Table 2, C21(carbene1)–Ln–C31(carbene2): 176.7(1)° (Nd), 177.6(3)° (Y)]. In accordance with the larger cation size the Nd–N [av. 2.388(2) Å] and N–C [av. 2.761(3) Å] bond lengths are longer than the corresponding ones in $Y[N(SiHMe_2)_2]_3(nhc)_2$ [Y–N: 2.288(6)–2.322(6) Å; Y–C: 2.648(8) and 2.671(9) Å].[7] For comparison, the Nd–C bond lengths in four-coordinate $(L)Nd[N(SiMe_3)_2]_2$ (L = amido-linked nhc)[20] and $Nd[N(SiMe_3)_2]_3(L')$ (L′ = 1,3,4,5-tetramethyl-2-methyleneimidazoline) are 2.609(3) and 2.691(6) Å, respectively.[21] The carbene ligands in $Ln[N(SiHMe_2)_2]_3(nhc)_2$ are slightly tilted and are arranged in a way that their mean square planes are almost perpendicular [87.6 (Y), 89.3° (Nd)].[21] The peculiar bonding fea-

Table 2. Selected bond lengths [Å], intramolecular distances [Å] and angles [°] for **4b**, **7b**, **7d**, and **8**.

4b		**7b**		**7d**		**8**	
Nd–N(1)	2.380(2)	Nd–N(1)	2.349(1)	Sc–N(1)	2.1135(7)	Y–N(1)	2.443(2)
Nd–N(2)	2.380(2)	Nd–N(2)	2.388(1)	Sc–N(2)	2.1366(7)	Y–N(2)	2.386(2)
Nd–N(3)	2.405(2)	Nd–N(3)	2.326(1)	Sc–N(3)	2.0840(7)	Y–N(3)	2.259(2)
Nd–C(21)*nhc*	2.771(3)	Nd–N(4)*phen*	2.6223(9)	Sc–N(4)*phen*	2.3779(7)	Y–N(4)	2.258(2)
Nd–C(31)*nhc*	2.751(3)	Nd–N(5)*phen*	2.652(1)	Sc–N(5)*phen*	2.3740(7)	Y···Si(1)	3.1863(7)
Nd···Si(1)	3.2511(8)	Nd···Si(1)	3.3255(3)	Sc···Si(2)	3.0359(3)	Y···Si(4)	3.1608(7)
Nd···Si(3)	3.305(1)	Nd···Si(4)	3.2055(4)	Sc···Si(4)	3.0467(3)	Y···Si(6)	3.0283(7)
Nd···Si(5)	3.287(9)	Nd···Si(6)	3.3540(4)	Sc···Si(6)	3.2119(3)	Y···Si(8)	3.0458(6)
						Li···Si(2)	2.917(4)
						Si(2)···H(2Si)	1.470(1)
Si(1)–N(1)–Si(2)	123.2(1)	Si(2)–N(1)–Si(1)	134.83(6)	Si(1)–N(1)–Si(2)	122.97(4)	Si(1)–N(1)–Si(2)	124.8(1)
Si(3)–N(2)–Si(4)	126.2(2)	Si(4)–N(2)–Si(3)	126.23(6)	Si(3)–N(2)–Si(4)	123.21(4)	Si(3)–N(2)–Si(4)	125.8(1)
Si(5)–N(3)–Si(6)	127.7(1)	Si(6)–N(3)–Si(5)	131.72(6)	Si(5)–N(3)–Si(6)	122.06(4)	Si(5)–N(3)–Si(6)	125.4(1)
Nd–N(1)–Si(1)	103.6(1)	Nd–N(1)–Si(2)	113.39(5)	Sc–N(1)–Si(1)	132.14(4)	Si(7)–N(4)–Si(8)	125.5(1)
Nd–N(1)–Si(2)	133.1(1)	Nd–N(1)–Si(1)	109.87(5)	Sc–N(1)–Si(2)	104.87(3)	Y–N(1)–Si(1)	98.52(8)
Nd–N(2)–Si(3)	107.5(1)	Nd–N(2)–Si(3)	130.85(5)	Sc–N(2)–Si(3)	132.24(4)	Y–N(1)–Si(2)	128.1(1)
Nd–N(2)–Si(4)	126.3(1)	Nd–N(2)–Si(4)	102.33(5)	Sc–N(2)–Si(4)	104.33(3)	Y–N(2)–Si(3)	129.7(1)
Nd–N(3)–Si(5)	106.5(1)	Nd–N(3)–Si(5)	116.11(5)	Sc–N(3)–Si(5)	122.34(4)	Y–N(2)–Si(4)	99.71(8)
Nd–N(3)–Si(6)	124.3(1)	Nd–N(3)–Si(6)	112.15(5)	Sc–N(3)–Si(6)	115.24(4)	Y–N(3)–Si(5)	135.7(1)
C(21)–Nd–C(31)	176.7(1)	N(4)–Nd–N(5)	62.38(3)	N(4)–Sc–N(5)	68.75(2)	Y–N(3)–Si(6)	98.85(9)
						Y–N(4)–Si(7)	133.8(1)
						Y–N(4)–Si(8)	99.93(9)

tures of the $N(SiHMe_2)_2$ ligands comprising distinct Nd–N–Si angles [e.g., Nd–N1–Si1: 103.6(1)°, Nd–N1–Si2: 133.2(1)°] as well as relatively short Nd···Si contacts [3.251(1)–3.305(1) Å] are indicative of Nd···H–Si β-agostic interactions.[22] Noteworthy is also the distinct bonding of the Si–N–Si fragments which are twisted out of the N1N2N3 plane by 32.5, 41.0, and 28.2°. This is in contrast to **2b** where due to the molecules *C*3 symmetry all three amido ligands are arranged in the same fashion (27°) and to **1b** exhibiting one large torsion angle (57.4°) and two smaller ones (7.6° and 16.4°).[2]

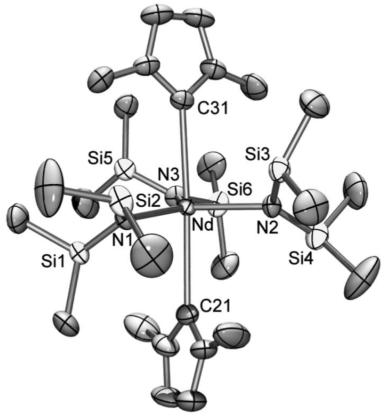


Figure 1. Molecular structure of $Nd[N(SiHMe_2)_2]_3(nhc)_2$ (**4b**) shown with atomic displacement parameters at the 50% level.

Like the bis(nhc) adducts, the complexes $Ln[N(SiHMe_2)_2]_3$-(phen) (Ln = Nd, **7b** and Sc, **7d**) crystallize in the same triclinic space group $P\bar{1}$. By nature, the strong chelating donor ligand enforces a different coordination geometry, which is best described as distorted square pyramidal (apical position occupied by N3). It is interesting that the phen donor accomplishes isostructural complexes for the large Nd^{3+} and small Sc^{3+} centers, albeit the phen bite angles differ significantly [68.75(2)° (Sc) and 62.38(3)° (Nd)]. The latter compares with those found for $Eu(dmp)_3$(2,9-di-

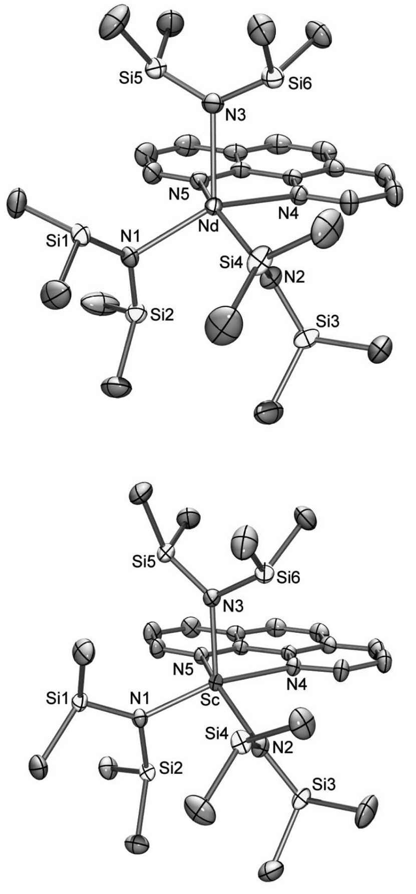


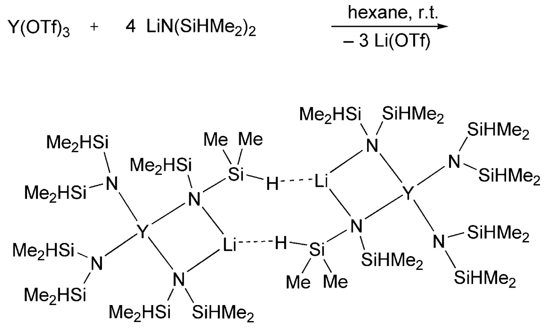
Figure 2. Molecular structures of $Sc[N(SiHMe_2)_2]_3$(phen) (**7d**, bottom) and $Nd[N(SiHMe_2)_2]_3$(phen) (**7b**, top) shown with atomic displacement parameters at the 50% level.

methyl-1,10-phenanthroline) [62.2(2)°, dmp = dipivaloylmethanato][23] and (2,2′:6′,2′′-terpyridine)$NdCl_3(H_2O)_8$ [62.69(7)°].[24] The Sc–N and Nd–N bond lengths in **7d** and **7b** range from 2.0840(7) to 2.1366(7) Å and 2.326(1) to 2.388(1) Å, respectively, and are significantly larger than the average Ln–N distances in the precursor compounds **1d** (2.069 Å) and **1b** (2.344 Å).[2] The twisting of the bis(dimethylsilyl) moieties out of the N1N2N3 planes is even more pronounced than in complexes **4** (**7b**: 13.20, 65.51, 74.13°; **7d**: 18.84, 50.08, 84.43°) and the asymmetric Ln–N–Si angles and close Ln···Si contacts are supportive of Ln···H–Si β-agostic interactions in the solid state (Table 2, Figure 2).

Synthesis and Characterization of an Yttrium *ate* Complex

Crucial details of our previously reported comprehensive synthesis protocol on $La[N(SiHMe_2)_2]_3(thf)_2$ were the high solvent dependency of the reaction outcome (thf vs. hexane) and the dependency on the precursor [$LaCl_3$ vs. $LaCl_3(thf)_{1.3}$ vs. $La(O_3SCF_3)_3$ = $La(OTf)_3$] as well as the nature of the alkali metal in $M[N(SiHMe_2)_2]$.[2] Use of $La(OTf)_3$ gave complicated product mixtures, while the corresponding reaction of $Y(OTf)_3$ with $LiN(SiHMe_2)_2$ was reported to yield $Y[N(SiHMe_2)_2]_3(thf)_2$ contaminated with a small amount of LiOTf.[2]

Isolation and full characterization of rare-earth metal bis(dimethylsilyl)amido ate complexes is still lacking, although Okuda et al. reported on the reaction of the lithium-containing scandium silylamide complex $Sc[N(SiHMe_2)_2]_3[LiN(SiHMe_2)_2(thf)]$ with 1,5-dithia-pentanediyl-bis(4,6-di-*tert*-butylphenol).[3g] Herein, we revisited the $Y(OTf)_3$–$Li[N(SiHMe_2)_2]$/hexane reaction (Scheme 2) and succeeded in obtaining single crystals of the donor solvent-free *ate* complex **8**.



8

Scheme 2. Synthesis of $\{Y[N(SiHMe_2)_2]_4Li\}_2$ **8** from yttrium(III) triflate in hexane.

The ambient temperature solution ^1H NMR spectrum of **8** displayed only one set of signals for the silylamido ligands. The Si*H* signal at δ = 4.78 ppm is shifted to higher field compared to $Y[N(SiHMe_2)_2]_3(thf)_2$ (**1e**) (δ = 4.99 ppm),[2] mixed amido/chloro complex $\{Y[N(SiHMe_2)_2]_2(\mu\text{-}Cl)(thf)\}_2$ (δ = 5.11 ppm),[25] or even homoleptic donor-free $\{Y[N(SiHMe_2)_2]_3\}_2$ (**9**, δ = 4.89 ppm).[26] The IR spectrum of complex **8** clearly suggests the occurrence of agostic interactions in the solid state, as indicated by the agostic shoulder at 1948 cm^{-1} (Table 1).

An X-ray structure analysis of **8** revealed the formation of $\{Y[N(SiHMe_2)_2]_4Li\}_2$ pairs featuring each two intermolecular Li···H–Si linkages (Figure 3).

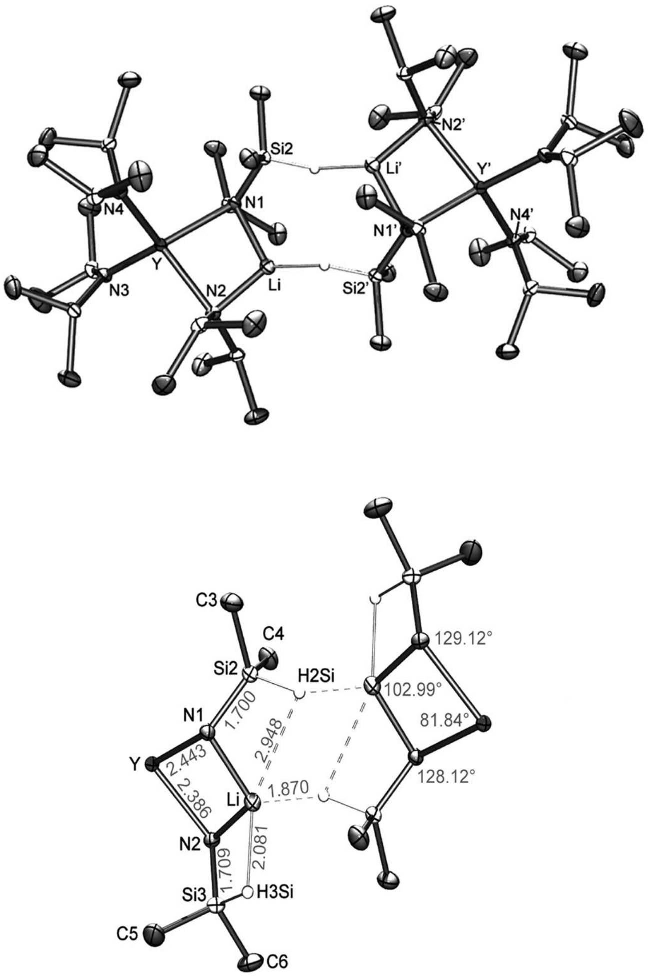


Figure 3. Molecular structure of $\{Y[N(SiHMe_2)_2]_4Li\}_2$ (**8**) shown with atomic displacement parameters at the 50% level (top); Li···Si–H secondary interactions in **8** causing dimerization; interatomic distances are given in Å (bottom). Symmetry operation for 2nd molecule is 1 – *x*, 2 – *y*, 1 – *z*.

The symmetrically bridged $\{Y[N(SiHMe_2)_2]_4\}^-Li^+$ units exhibit Y–N bond lengths ranging from 2.258(2) to 2.443(2) Å, which lie in the expected range of other yttrium bis(dimethylsilyl)amido complexes.[2,25,26] For comparison the Y–N bond lengths in homoleptic donor-free **9** (terminal: av. 2.249 Å; bridging: av. 2.479 Å),[26] **1e** [2.229(4)–2.276(4) Å],[2] and the mixed amido/chloro complex $\{Y[N(SiHMe_2)_2]_2(\mu\text{-}Cl)(thf)\}_2$ (av. 2.231 Å)[25] range from 2.211(2) to 2.504(2) Å. All of the four silylamido ligands in **8** participate in Y···H–Si β-agostic interactions as indicated by asymmetric Y–N–Si angles and Y···Si contacts as close as 3.0283(7) Å. The latter are as short as the ones detected in the *ansa* yttrocene amide complex *rac*-[Me_2Si(2-Me-Benz-Ind)$_2$]Y[N($SiHMe_2$)$_2$] [3.028(1) Å][27] or **9** [3.0521(7) Å].[26] The most striking structural feature of complex **8** is the environment of the formally four-coordinate Li^+ cations. One of the dimethyl silyl groups of each bridging amido ligand (N1/2) engages in distinct Li···H–Si interactions – one "strained" intramolecular agostic with a Li···H distance of 2.08(1) Å and one intermolecular with a relatively short Li···H contact of 1.87(1) Å. These Li···H interactions compare to those in (Me_3Si)$_2$NSi(H)[N-(Li)$SiMe_3$]$_2$ (Li···H: 1.89–1.91 Å),[28] {Li[μ-N($SiMe_3$)-($SiHtBu_2$)]}$_2$ (av. Li···H: 2.05 Å)[29] and {Li[μ-N(CMe_3)-($SiHtBu_2$)]}$_2$ (av. Li···H: 2.07 Å).[29] It is well known that sterically unsaturated rare-earth metal silylamide complexes tend to complete their coordination sphere by formation of Ln···H–Si or Ln···CH_3–Si agostic interactions.[30] For example, donor- and ate-free complex {Y[N($SiHMe_2$)$_2$]$_3$} (**9**) has also a dimeric molecular composition, {Y[N($SiHMe_2$)$_2$]$_2$[μ-N($SiHMe_2$)$_2$]}$_2$, while steric saturation is not only accomplished by asymmetrically bridging silylamido ligands but also by Y···Si–H multi-agostic interactions (in the solid state).[26] Moreover, agostic M···H–Si contacts are also found in alkali metal silylamide complexes.[31–33] While in [LiN($SiHMe_2$)*t*Bu]$_3$ such Li···H–Si interactions seem to be present only in solution,[31] the infinite all-planar ladder structure of [NaN($SiHMe_2$)$_2$]$_n$ reveals Na···H–Si interactions in the solid state.[32]

Conclusions

Easy exchange of the thf ligands in Ln[N($SiHMe_2$)$_2$]$_3$-(thf)$_n$ by mono- and bifunctional donor molecules corroborates the ready accessibility of the rare-earth metal centers and, hence, the versatility of these discrete amide complexes as synthesis precursors. FTIR and ^1H NMR spectroscopic investigations of the SiH functionality in derivatives La[N-($SiHMe_2$)$_2$]$_3$(donor)$_x$ suggests a distinct donor capability in the order thf < 1,3-dimethylimidazolin-2-ylidene < *N*-methylimidazole < triphenylphosphane oxide < 1,10-phenanthroline. Coordination of the latter bifunctional donor ligand involves a geometry switch from distorted trigonal bipyramidal (metal size-dependent) to distorted square pyramidal (metal size-independent). In the absence of donor solvent molecules and presence of alkali metal bis(dimethylsilylamido) complexes [here LiN($SiHMe_2$)$_2$] ate complex formation displays an alternative (and predominant) pathway for the Ln^{3+} metal center to achieve stereoelectronic saturation. In {Y[N($SiHMe_2$)$_2$]$_4$Li}$_2$, the Li^+ ions are not fully embedded into the hydrophobic periphery of the bridging amido ligands but form very short intermolecular Li···H–Si contacts.

Experimental Section

General: All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum and glovebox techniques. Solvent pretreatment/purification was performed with Grubbs columns (MBraun SPS, solvent purification system) or refluxed over Na/K alloy. C_6D_6 was obtained from Deutero GmbH or Aldrich, degassed, dried with Na for 24 h, filtered, and stored in a glovebox. LiN($SiHMe_2$)$_2$ was prepared by reacting HN($SiHMe_2$)$_2$ (Aldrich) with *n*-butyllithium (Aldrich) in hexane. 1,2-bis(dimethylphosphanyl)ethane, 1,2-Bis(diphenylphosphanyl)ethane, potassium hydride, *N*-methylimidazole, 1,10-phenanthroline, *N*,*N*,*N′*,*N′*-tetramethylethylenediamine, triphenylphosphane oxide, and yttrium(III) trifluoromethanesulfonate were purchased from Aldrich. The latter Y(OTf)$_3$ was fully dehydrated in high vacuum at 180 °C overnight. Sc[N($SiHMe_2$)$_2$]$_3$(THF),[2] Ln[N($SiHMe_2$)$_2$]$_3$-(THF)$_2$ (Ln = La, Nd, Pr)[1,2] and 1,3-dimethylimidazolin-2-ylidene[14] were synthesized according to literature procedures. NMR spectroscopic data were obtained in C_6D_6 solution at 25 °C from a FT-JEOL-JNM-GX-400 (^1H: 399.80 MHz; ^{13}C: 100.51 MHz, ^{31}P: 161.80 MHz), a Bruker-BIOSPIN-AV500 (5 mm BBO, ^1H: 500.13 MHz; ^{13}C: 125.77 MHz), and a FT-JEOL-JNM-GX-270 (^1H: 270 MHz; ^{13}C: 67.5 MHz) spectrometer. ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Perkin–Elmer spectrometer 1650-FTIR or a Jasco FT/IR – 460 Plus spectrometer using Nujol mulls sandwiched between CsI plates. Mass spectra were recorded on a Finnigan-MAT 90. Elemental analyses were performed in the microanalytical laboratory of the Technische Universität München or on an Elementar Vario EL III.

***trans*-Bis(triphenylphosphane oxide)tris[bis(dimethylsilyl)amido]lanthanum(III), -neodymium(III) and -praseodymium(III) (2a–c):** Ln[N($SiHMe_2$)$_2$]$_3$(thf)$_2$ (Ln = La, Pr, Nd; 1 equiv.) and triphenylphosphane oxide (2 equiv.) were stirred in a *n*-hexane/toluene mixture for 12 h at ambient temperature and for an additional hour at 60 °C. During the reaction a precipitate formed continuously and was removed by centrifugation. The solvent was removed under vacuum and the resulting powder recrystallized from toluene.

La[N($SiHMe_2$)$_2$]$_3$(*O*=PPh_3)$_2$ (2a): La[N($SiHMe_2$)$_2$]$_3$(thf)$_2$ (340 mg, 0.50 mmol), O=PPh_3 (278 mg, 1.00 mmol), *n*-hexane (7.5 mL), toluene (1.5 mL); white powder; yield 481 mg (0.44 mmol, 88 %). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.89 (m, 12 H, Ph), 7.18 (m, 12 H, Ph), 7.09 (m, 6 H, Ph), 5.30 [h, ^3J(H,H) = 2.72 Hz, 6 H, SiH], 0.28 [d, ^3J(H,H) = 2.72 Hz, 36 H, $SiCH_3$] ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): δ = 133.3 [d, ^2J(C,P) = 10.68 Hz, $C^{Ph,ortho}$], 132.7 (s, $C^{Ph,para}$), 130.5 [d, ^1J(C,P) = 108.84 Hz, $C^{Ph,ipso}$], 128.7 [d, ^3J(C,P) = 12.64 Hz, $C^{Ph,meta}$], 3.6 (s, $SiCH_3$) ppm. ^{31}P NMR (161.8 MHz, C_6D_6, 20 °C): δ = 35.1 ppm. IR: $\tilde{\nu}_{max}$ = 2016 (vs, [ν(SiH)]), 1960 (w, sh), 1913 (w), 1892 (w), 1815 (w), 1777 (w), 1770 (w), 1591 (m), 1438 (s), 1236 (s), 1154 (s), 1122 (s), 1090 (m), 1065 (w), 1032 (vs), 997 (m), 943 (s), 898 (vs), 894 (m), 824 (m), 785 (m), 761 (m), 742 (m), 691 (s), 639 (w), 601 (m), 541 (s), 511 (w), 498 (w), 494 (w) cm^{-1}. MS (CI): *m*/*z* (%) = 1092 (2) [M^+], 1076 (6) [M^+ – CH_4], 1034 (4) [M^+ – Si(CH_3)$_2$], 958 (100) [M^+ – HN($SiHMe_2$)$_2$], 826 (5) [M^+ – 2 HN($SiHMe_2$)$_2$], 278 (29) [O=PPh_3(H)]. $C_{48}H_{72}LaN_3O_2P_2Si_6$ (1092.49 g mol^{-1}): calcd. C 52.77, H 6.64, N 3.85; found C 52.15, H 6.81, N 3.48.

Nd[N($SiHMe_2$)$_2$]$_3$(*O*=PPh_3)$_2$ (2b): Nd[N($SiHMe_2$)$_2$]$_3$(thf)$_2$ (343 mg, 0.50 mmol), O=PPh_3 (278 mg, 1.00 mmol), *n*-hexane (7.5 mL), toluene (1.5 mL); light blue powder; yield 474 mg (0.43 mmol, 86 %). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 10.40 (s, 6 H, SiH), 6.61 (s, 18 H, Ph), 5.00 (s, 12 H, Ph), 2.02 (s, 36 H, $SiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): δ = 131.9 (s, $C^{Ph,para}$), 130.4 [d, ^2J(C,P) = 5.84 Hz, $C^{Ph,ortho}$], 127.3 [d, ^3J(C,P) = 11.66 Hz, $C^{Ph,meta}$], 122.0 [d, ^1J(C,P) ≈ 100 Hz, $C^{Ph,ipso}$], 13.8 (s, $SiCH_3$) ppm. ^{31}P NMR (161.8 MHz, C_6D_6, 20 °C): δ = 116.5 ppm. IR: $\tilde{\nu}_{max}$ = 2063 (s, sh), 2040 (s), 2018 [vs, ν(SiH)], 1963 (m, sh), 1913 (w), 1892 (w), 1817 (w), 1771 (w), 1591 (m), 1438 (s), 1336 (w), 1312 (w), 1235 (s), 1155 (s), 1121 (s), 1091 (m), 1070 (m), 1058 (m), 1026 (s), 935 (s), 893 (vs), 832 (s), 780 (m), 760 (m), 743 (m), 691 (s), 639 (w), 605 (m), 540 (s), 507 (w), 496 (w), 449 (w) cm^{-1}. MS (CI): *m/z* (%) = 1098 (6) [M$^+$], 1096 (15) [M$^+$ – 24], 1082 (16) [M$^+$ – CH$_4$], 1039 (2) [M$^+$ – HSi(CH$_3$)$_2$], 963 (60) [M$^+$ – HN(SiHMe$_2$)$_2$ – 2 H], 832 (6) [M$^+$ – 2 HN(SiHMe$_2$)$_2$], 820 (2) [M$^+$ – O=PPh$_3$], 542 (3) [M$^+$ – 2 O=PPh$_3$], 132 (6) [N(SiHMe$_2$)$_2$]. C$_{48}$H$_{72}$N$_3$NdO$_2$P$_2$Si$_6$ (1097.83 g mol^{-1}): calcd. C 52.52, H 6.61, N 3.83; found C 51.99, H 6.45, N 3.61.

Pr[N(SiHMe$_2$)$_2$]$_3$(O=PPh$_3$)$_2$ (2c): Pr[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (682 mg, 1.00 mmol), O=PPh$_3$ (559 mg, 2.01 mmol), *n*-hexane (15 mL), toluene (3 mL); off-white powder; yield 974 mg (0.89 mmol, 89%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 8.12 (s, 6 H, SiH), 6.41 (s, 18 H, Ph), 3.98 (s, 12 H, Ph), 2.30 (s, 36 H, SiCH$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 131.5 (s, C$^{\text{Ph},para}$), 129.3 (s, C$^{\text{Ph},ortho}$), 126.9 [d, ^3J(C,P) = 6.8 Hz, C$^{\text{Ph},meta}$], 120.8 [d, ^1J(C,P) ≈ 100 Hz, C$^{\text{Ph},ipso}$], 12.4 (s, SiCH$_3$) ppm. IR: $\tilde{\nu}_{\max}$ = 2018 [vs, ν(SiH)], 1959 (s, sh), 1912 (w), 1895 (w), 1814 (w), 1774 (w), 1591 (m), 1485 (m), 1438 (s), 1335 (w), 1340 (w), 1235 (s), 1154 (s), 1120 (s), 1089 (s), 1068 (m), 1026 (vs), 999 (s), 941 (vs, br.), 899 (vs, br.), 831 (vs), 790 (s), 761 (s), 692 (s), 640 (s), 604 (s), 541 (vs), 449 (m) cm^{-1}. MS (CI): *m/z* (%) = 1092 (3) [M$^+$ – 2 H], 1078 (3) [M$^+$ – CH$_4$], 816 (3) [M$^+$ – O=PPh$_3$], 961 (66) [M$^+$ – HN(SiHMe$_2$)$_2$], 828 (12) [M$^+$ – 2 HN(SiHMe$_2$)$_2$], 132 (7) [HN(SiHMe$_2$)$_2$]. C$_{48}$H$_{72}$N$_3$O$_2$P$_2$PrSi$_6$ (1094.47 g mol^{-1}): calcd. C 52.68, H 6.63; N 3.84; found C 52.34, H 6.63; N 3.55%.

***trans*-Bis(*N*-methylimidazole)tris[bis(dimethylsilyl)amido]lanthanum(III) and -neodymium(III) (3a,b):** Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (Ln = La, Nd; 0.50 mmol) and 1-methylimidazole (82.3 mg, 1.00 mmol) were stirred in a mixture of *n*-hexane (7.5 mL) and toluene (1.5 mL) for 12 h at ambient temperature and then for an additional hour at 60 °C. During the reaction a fluffy precipitate formed which was removed by centrifugation and the resulting powder dried under vacuum.

La[N(SiHMe$_2$)$_2$]$_3$(*N*-MeIm)$_2$ (3a): La[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (340 mg) yielded 238 mg of **3a** (0.34 mmol, 68%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.69 (br. s, 2 H, CH), 7.45 (br. s, 2 H, CH), 6.05 (br. s, 2 H, CH), 5.26 [h, ^3J(H,H) = 3.04 Hz, 6 H, SiH], 2.42 (br. s, 6 H, NCH$_3$), 0.43 [d, ^3J(H,H) = 3.04 Hz, 36 H, SiCH$_3$] ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25 °C): δ = 126.1, 124.9, 122.7 (all CH), 21.9 (NCH$_3$), 3.3 (SiCH$_3$) ppm.

Nd[N(SiHMe$_2$)$_2$]$_3$(*N*-MeIm)$_2$ (3b): Nd[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (343 mg) yielded 240 mg of **3b** (0.34 mmol, 71%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 13.00 (br. s, 6 H, SiH), 4.02 (s, 36 H, SiCH$_3$), 2.10 (m, 6 H, NCH$_3$), 1.22 ("m", 2 H, CH), 0.84 ("m", 2 H, CH), 0.10 ("m", 2 H, CH) ppm. IR: $\tilde{\nu}_{\max}$ = 2046 [vs, ν(SiH)], 1792 (w), 1653 (w), 1580 (w), 1528 (m), 1515 (m), 1496 (w), 1420 (m), 1284 (m), 1240 (s), 1110 (m), 1057 (s), 894 (s), 833 (s), 782 (s), 759 (s), 678 (m), 659 (m), 645 (m), 596 (m), 464 (w) cm^{-1}.

***trans*-Bis(1,3-dimethylimidazolin-2-ylidene)tris[bis(dimethylsilyl)amido]lanthanum(III) and -neodymium(III) (4a,b):** 1,3-Dimethylimidazolium iodide (224 mg, 1.00 mmol) was suspended in thf (15 mL) and treated with potassium hydride (40 mg, 1.00 mmol) and potassium *tert*-butoxide (5.6 mg, 0.05 mmol). The reaction mixture was stirred at ambient temperature until gas evolution (H$_2$) stopped, while the solvent turned light yellow and a white precipitate formed. The solution was separated from the precipitate and immediately Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (0.50 mmol) in thf (5 mL) added dropwise. When no more color change was observed (ca. 1 h) the solvent was removed under vacuum and the resulting powder extracted with *n*-hexane. Crystals could be obtained at –35 °C from saturated hexane solutions.

La[N(SiHMe$_2$)$_2$]$_3$(nhc)$_2$ (4a): La[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (373 mg, 0.55 mmol) yielded a yellow crystalline powder of **4a** (310 mg, 0.43 mmol, 85%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 6.03 (s, 4 H, HC=CH), 5.13 [h, ^3J(H,H) = 2.96 Hz, 6 H, SiH], 3.71 (s, 12 H, NCH$_3$), 0.27 [d, ^3J(H,H) = 2.96 Hz, 36 H, SiCH$_3$] ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 120.4 (HC=CH), 38.2 (NCH$_3$), 3.2 (SiCH$_3$) ppm. IR: $\tilde{\nu}_{\max}$ = 2062 /2044 [vs, ν(SiH)], 1243 (m), 1217 (w), 1166 (w), 1050 (m), 896 (s), 833 (m), 773 (w), 759 (w), 677 (w), 595 (w), 444 (w) cm^{-1}. MS (CI): *m/z* (%) = 728 (2) [M$^+$], 713 (16) [M$^+$ – CH$_3$], 632 (17) [M$^+$ – carbene – H], 596 (47) [M$^+$ – N(SiHMe$_2$)$_2$], 536 (8) [M$^+$ – 2 carbene], 500 (100) [M$^+$ – carbene – N(SiHMe$_2$)$_2$], 403 (8) [M$^+$ – 2 carbene – HN(SiHMe$_2$)$_2$], 132 (36) [N(SiHMe$_2$)$_2$]. C$_{22}$H$_{58}$LaN$_7$Si$_6$ (728.17 g mol^{-1}): calcd. C 36.29, H 8.03, N 13.46; found C 35.74, H 7.96, N 12.83.

Nd[N(SiHMe$_2$)$_2$]$_3$(nhc)$_2$ (4b): Nd[N(SiHMe$_2$)$_2$]$_3$ (thf)$_2$ (372.7 mg, 0.54 mmol) yielded a green crystalline powder of **4b** (253 mg, 0.35 mmol, 69%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.62 (br. s, 6 H, SiH), 5.56 (s, 4 H, HC=CH), 2.57 (br. s, 36 H, 12 H, SiCH$_3$, NCH$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 16.9 (SiCH$_3$, remaining signals could not be assigned) ppm. IR: $\tilde{\nu}_{\max}$ = 2069/2039 [vs, ν(SiH)], 1245 (m), 1216 (w), 1169 (w), 1046 (m), 972 (w), 939 (m), 896 (s), 833 (m), 777 (m), 759 (m), 720 (m), 690 (w), 676 (w), 594 (w), 444 (w) cm^{-1}. MS (CI): *m/z* (%) = 734 (3) [M$^+$], 718 (2) [M$^+$ – CH$_4$], 636 (13) [M$^+$ – carbene – 2 H], 601 (47) [M$^+$ – HN(SiHMe$_2$)$_2$], 542 (7) [M$^+$ – 2 carbene], 505 (7) [M$^+$ – carbene – HN(SiHMe$_2$)$_2$], 132 (36) [N(SiHMe$_2$)$_2$]. C$_{22}$H$_{58}$N$_7$NdSi$_6$ (733.50 g mol^{-1}): calcd. C 36.03, H 7.97, N 13.97; found C 36.04, H 8.06, N 12.71.

[1,2-Bis(dimethylphosphanyl)ethane]tris[bis(dimethylsilyl)amido]neodymium(III) (5): A solution of Nd[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (685 mg, 1.00 mmol) and 1,2-bis(dimethylphosphanyl)ethane (150 mg, 1.00 mmol) in *n*-hexane (10 mL) was heated to 60 °C for 20 min under continuous stirring. After stirring for additional 12 h at ambient temperature and removal of the volatile products a light blue crystalline powder of Nd[N(SiHMe$_2$)$_2$]$_3$(dmpe) (**5**) was obtained (470 mg, 0.68 mmol, 68%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 7.26 (s, 4 H, CH$_2$), 4.73 ("d", 36 H, SiCH$_3$), 1.08 ("d", 6 H, SiH), –1.92 (s, 12 H, PCH$_3$) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25 °C): δ = 20.9 (SiCH$_3$), 14.8 (PCH$_3$), 13.6 (CH$_2$) ppm. IR: $\tilde{\nu}_{\max}$ = 2049 [vs, ν(SiH)], 2000 (s, sh), 1300 (w), 1245 (m), 1146 (w), 1052 (s), 943 (m), 897 (s), 834 (m), 784 (m), 761 (m), 681 (w), 625 (w), 595 (w) cm^{-1}. MS (CI): *m/z* (%) = 541 (2) [M$^+$ – dmpe], 525 (5) [M$^+$ – dmpe – CH$_4$], 407 (84) [M$^+$ – dmpe – H$_2$N(SiHMe$_2$)$_2$], 132 (22) [N(SiHMe$_2$)$_2$], 118 (71) [(SiHMe$_2$)$_2$]. C$_{18}$H$_{58}$N$_3$NdP$_2$Si$_6$ (691.38 g mol^{-1}): calcd. C 31.27, H 8.46, N 6.08; found C 30.93, H 8.70, N 5.24.

(*N*,*N*,*N*′,*N*′-Tetramethylethylendiamine)tris[bis(dimethylsilyl)amido]lanthanum(III) (6): To a solution of La[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$ (680 mg, 1.00 mmol) in *n*-hexane (10 mL) tmeda (116 mg, 1.00 mmol) was added and the resulting solution stirred at ambient temperature for 72 h. Removal of the volatile products under vacuum gave 365 mg of La[N(SiHMe$_2$)$_2$]$_3$(tmeda) as a white powder (0.56 mmol, 56%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 5.03 [h, ^3J(H,H) = 3.0 Hz, 6 H, SiH], 2.16 (s, 12 H, NCH$_3$), 1.76 (s, 4 H, CH$_2$), 0.41 [d, ^3J(H,H) = 3.0 Hz, 36 H, SiCH$_3$] ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 25 °C): δ = 57.8 (CH$_2$), 47.7 (NCH$_3$), 3.5 (SiCH$_3$) ppm. IR: $\tilde{\nu}_{\max}$ = 2046 /2017 [vs, ν(SiH)], 1778 (w), 1666 (w), 1280 (m), 1240 (s), 1182 (w), 1160 (w), 1128 (w), 1081 (s), 1048 (s), 1033 (m), 947 (s), 894 ((vs)), 834 (s), 779 (s), 759 (m), 698 (m), 677 (m), 625 (w), 593 (m), 495 (w), 439 (w) cm^{-1}. MS (CI): *m/z* (%)

= 652 (2) [M^+], 534 (100) [M^+ – tmeda – 2H], 403 (3) [M^+ – tmeda – HN($SiHMe_2)_2$], 132 (22) [N($SiHMe_2)_2$], 118 (71) [($SiHMe_2)_2$]. $C_{18}H_{58}LaN_5Si_6$ (652.11 $g\,mol^{-1}$): calcd. C 33.15, H 8.96, N 10.74; found C 33.08, H 8.79, N 9.61.

(1,10-Phenanthroline)tris[bis(dimethylsilyl)amido]scandium(III), -lanthanum(III) and -neodymium(III)(7a,b,d): To Ln[N($SiHMe_2)_2]_3$(thf)$_n$ (1.00 mmol) in toluene (10 mL) a solution of 1,10-phenanthroline (180 mg, 1.00 mmol) in toluene (5 mL) was added dropwise at ambient temperature and stirred at 40 °C for 12 h. Complete reaction was indicated by the formation of a deep purple solution. After removal of the volatile products under vacuum a light purple powder was obtained. Complexes **7a**,**b**,**d** were crystallized from saturated thf/*n*-hexane solutions at –35 °C.

Sc[N($SiHMe_2)_2]_3$(phen) (7d): Sc[N($SiHMe_2)_2]_3$(thf) (136 mg, 0.27 mmol) yielded 147 mg of **7d** (0.24 mmol, 89%). ^1H NMR (500 Hz, C_6D_6, 25 °C): δ = 9.94 [dd, ^3J(H,H) = 5.0, ^4J(H,H) = 1.5 Hz, 2 H, $H^{2,Phen}$, $H^{9,Phen}$], 7.32 [dd, ^3J(H,H) = 8.0, ^4J(H,H) = 1.5 Hz, 2 H, $H^{4,Phen}$, $H^{7,Phen}$], 6.94 (s, 2 H, $H^{5,Phen}$, $H^{6,Phen}$), 6.92 [dd, ^3J(H,H) = 5.0, ^3J(H,H) = 8.0 Hz, 2 H, $H^{3,Phen}$, $H^{8,Phen}$], 5.34 [h, ^3J(H,H) = 3.0 Hz, 6 H, SiH], 0.31 [d, ^3J(H,H) = 3.0 Hz, 36 H, $SiCH_3$] ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 153.9, 144.0, 138.7, 128.6, 126.3, 123.8 (C^{Phen}), 3.1 ($SiCH_3$) ppm. IR: $\tilde{\nu}_{max}$ = 2108 [vs, ν(SiH)], 2076 ((vs)), 2016 (vs), 1627 (w), 1589 (w), 1577 (w), 1519 (m), 1422 (s), 1346 (s), 1239 (vs), 1105 (w), 1022 (vs), 991 (s), 927 (vs), 885 (vs), 836 (vs), 791 (s), 761 (s), 695 (s), 677 (m), 639 (m), 628 (m), 439 (w), 421 (w), 404 (w) cm^{-1}. $C_{24}H_{50}N_5ScSi_6$ (622.16 $g\,mol^{-1}$): calcd. C 46.33, H 8.10, N 11.26; found C 46.46, H 7.93, N 10.70.

La[N($SiHMe_2)_2]_3$(phen) (7a): La[N($SiHMe_2)_2]_3(thf)_2$ 680 mg (1.00 mmol) yielded 665 mg **7a** (0.93 mmol, 93%). ^1H NMR (399.8 MHz, C_6D_6, 25 °C): δ = 9.69 [dd, ^3J(H,H) = 4.76, ^4J(H,H) = 1.83 Hz, 2 H, $H^{2,Phen}$, $H^{9,Phen}$], 7.32 [dd, ^3J(H,H) = 8.08, ^4J(H,H) = 1.83 Hz, 2 H, $H^{4,Phen}$, $H^{7,Phen}$], 6.92 (s, 2 H, $H^{5,Phen}$, $H^{6,Phen}$), 6.91 [dd, ^3J(H,H) = 4.76, ^3J(H,H) = 8.08 Hz, 2 H, $H^{3,Phen}$, $H^{8,Phen}$], 5.23 [h, ^3J(H,H) = 2.93 Hz, 6 H, SiH], 0.34 [d, ^3J(H,H) = 2.93 Hz, 36 H, $SiCH_3$] ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 151.9, 145.0, 138.2, 128.9, 126.4, 123.4 (C^{Phen}), 2.8 ($SiCH_3$) ppm. IR: $\tilde{\nu}_{max}$ = 2039 [vs, [ν(SiH)]], 1923 (sh), 1624 (w), 1589 (w), 1574 (w), 1516 (m), 1312 (m), 1239 (s), 1100 (s), 1078 (s), 985 (m), 931 (m), 904 (s), 885 (s), 833 (s), 780 (m), 760 (m), 729 (m), 682 (w), 636 (w), 623 (w), 579 (w) cm^{-1}. MS (CI): *m*/*z* (%) = 714 (2) [M^+ – H], 583 (16) [M^+ – N($SiHMe_2)_2$], 535 (1) [M^+ – phen], 451 (1) [M^+ – 2 N($SiHMe_2)_2$], 402 (14) [M^+ – phen – HN($SiHMe_2)_2$], 132 (43) N($SiHMe_2)_2$], 118 (100) ($SiHMe_2)_2$]. $C_{24}H_{50}LaN_5Si_6$ (715.17 $g\,mol^{-1}$): calcd. C 40.27, H 7.05, N 9.79; found C 38.94, H 6.02, N 7.44.

Nd[N($SiHMe_2)_2]_3$(phen) (7b): Nd[N($SiHMe_2)_2]_3(thf)_2$ (686 mg, 1.00 mmol) yielded 642 mg **7b** (0.89 mmol, 89%). ^1H NMR (399.8 MHz, C_6D_6, 25 °C): δ = 11.60 (s, 2 H, $H^{2,Phen}$, $H^{9,Phen}$), 6.02 [d, ^3J(H,H) = 8.06 Hz, 2 H, $H^{4,Phen}$, $H^{7,Phen}$], 4.66 [d, ^3J(H,H) = 8.06 Hz, 2 H, $H^{3,Phen}$, $H^{8,Phen}$], 4.26 (s, 36 H, $SiCH_3$), 3.56 (s, 2 H, $H^{5,Phen}$, $H^{6,Phen}$), –1.03 (s, 6 H, SiH) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 131.0, 127.3, 122.0, 115.0, 110.2, 52.9 (alle C^{Phen}), 18.6 ($SiCH_3$) ppm. IR: $\tilde{\nu}_{max}$ = 2060 [vs, [ν(SiH)]], 1939 (m, sh), 1625 (w), 1589 (w), 1575 (w), 1540 (w), 1516 (m), 1506 (w), 1346 (m), 1312 (m), 1239 (vs), 1142 (m), 1106 (m), 1085 (s), 1062 (s), 976 (s), 931 (s), 905 (s), 886 (s), 833 (s), 782 (s), 760 (s), 729 (m), 681 (m), 637 (m), 588 (m) cm^{-1}. MS (CI): *m*/*z* (%) = 721 (9) [M^+], 589 (100) [M^+ – N($SiHMe_2)_2$], 541 (3) [M^+ – phen], 457 (5) [M^+ – 2 N($SiHMe_2)_2$], 408 (8) [M^+ – phen – HN($SiHMe_2)_2$], 132 (3) N($SiHMe_2)_2$], 118 (5) ($SiHMe_2)_2$]. $C_{24}H_{50}N_5NdSi_6$ (721.45 $g\,mol^{-1}$): calcd. C 39.96, H 6.99, N 9.71; found C 38.71, H 6.12, N 7.59.

{Y[N($SiHMe_2)_2]_4Li\}_2$ (8): $Y(OTf)_3$ (199 mg, 0.37 mmol) and 4 equiv. of LiN($SiHMe_2)_2$ (206 mg) were suspended in hexane and stirred at ambient temperature for 24 h. The reaction mixture was centrifuged and the separated hexane solution additionally filtered. After evaporation of the solvent a white powder was obtained. Further crystallization from a saturated hexane solution yielded **8** as colorless crystals (177 mg, 0.14 mmol, 77%). ^1H NMR (500 Hz, C_6D_6, 25 °C): δ = 4.78 [h, ^3J(H,H) = 2.5 Hz, 8 H, SiH], 0.48 [d, ^3J(H,H) = 2.5 Hz, 36 H, $SiCH_3$] ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C): δ = 3.3 ($SiCH_3$) ppm. IR: $\tilde{\nu}_{max}$ = 2065 [vs, ν(SiH)], 1948 (sh), 1249 (vs), 1040 (s), 896 (vs, br.), 838 (s), 788 (s), 765 (s), 683 (w), 459 (w), 432 (w), 410 (w) cm^{-1}. $C_{32}H_{112}Li_2N_8Si_{16}Y_2$ (1250.35 $g\,mol^{-1}$): calcd. C 30.74, H 9.03, N 8.96; found C 30.56, H 9.31, N 8.29.

Crystallography: Crystals of **4b**, **7b**, **7d** and **8** were grown by standard techniques from saturated solutions using *n*-hexane or thf/*n*-hexane at –35 °C. Suitable single crystals were selected in a

Table 3. Crystallographic data for Nd[N($SiHMe_2)_2]_3(nhc)_2$ (**4b**), Sc[N($SiHMe_2)_2]_3$(phen) (**7d**), Nd[N($SiHMe_2)_2]_3$(phen) (**7b**) and {Y[N($SiHMe_2)_2]_4Li\}_2$ (**8**).

	4b	**7d**	**7b**	**8**
Chemical formula	$C_{22}H_{58}N_7NdSi_6$	$C_{24}H_{50}N_5ScSi_6$	$C_{24}H_{50}N_5NdSi_6$	$C_{32}H_{112}Li_2N_8Si_{16}Y_2$
M_r	733.53	622.19	721.47	1250.22
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.1559(6)	11.6602(4)	11.3973(4)	10.8694(4)
b [Å]	11.6882(6)	11.9924(5)	12.4489(4)	11.2793(4)
c [Å]	17.1805(9)	12.5809(5)	13.1690(5)	16.5333(7)
α [°]	78.917(5)	86.199(1)	95.408(1)	84.934(1)
β [°]	86.304(6)	89.201(1)	90.453(1)	77.088(1)
γ [°]	62.082(5)	83.068(1)	99.624(1)	64.328(1)
V [$Å^3$]	1941.7(2)	1742.50(12)	1833.44(11)	1780.61(12)
Z	2	2	2	1
F(000)	766	668	746	668
T [K]	193	123	123	123
ρ_{calcd} [$g\,cm^{-3}$]	1.255	1.186	1.307	1.166
μ [mm^{-1}]	1.544	0.439	1.632	1.918
R_1[a] (obsd.), wR_2[b] (all)	0.0234, 0.0596	0.0245, 0.0755	0.0161, 0.0436	0.0312, 0.0758
S[c]	0.998	1.012	1.094	1.093

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $F_o > 4\sigma(F_o)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2}$.

glovebox, coated with Paratone-N, fixed in a nylon loop, mounted on a Bruker SMART 2 K CCD diffractometer (**7b**, **7d**, **8**), or coated with perfluorinated polyether, fixed in a glass capillary and mounted on a STOE IPDS diffractometer (**4b**). X-ray diffraction data were collected using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and ω-scans (**7b**, **7d**, **8**), ϕ-scan (**4b**).[34,35]. Raw data were reduced and scaled with programs SAINT[35] (**7b**, **7d**, **8**) and DENZO[36] (**4b**) and corrections for absorption effects were applied using SHELXTL[37] (**7b**, **7d**, **8**). The structures were solved by a combination of direct methods (SHELXS[38] and SIR92[39]) and difference-Fourier syntheses (SHELXL-97[38]). All non-hydrogen atoms were refined anisotropically. Further details of the refinement and crystallographic data are listed in Table 3. All plots were generated using the program ORTEP-3.[40] CCDC-674049-674052 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.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG) (SPP 1166) and the program NANOSCIENCE@UiB for generous support.

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Received: January 15, 2008