The Substitution Reaction of (Chloro)bis(tetraisopropylcyclopentadienyl) Complexes of La, Pr, or Nd with Silylamides

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The dimeric complexes $[\{(C_5HR_4)_2Ln(\mu\text{-}Cl)(\mu_3\text{-}Cl)Na(OEt_2)\}_2]$ (**1**) (R = $CHMe_2$, Ln = La, Pr, Nd) eliminate sodium chloride in toluene solution to form the (chloro)bis(cyclopentadienyl) complexes $[(C_5HR_4)_2LnCl]$ (**2**). Crystalline **2**-Nd contains monomeric molecules exhibiting two intramolecular Nd···CH_3 interactions (Nd···C = 3.32 Å) with ring substituents. Reaction of complexes **1** with bis(trimethylsilyl)amides furnishes the tetranuclear complexes $[\{(C_5HR_4)_2Ln(\mu\text{-}Cl)\}_2\{NaN(SiMe_3)_2\}_2]$ (**3**) (R = $CHMe_2$, Ln = La, Pr, Nd), which have been characterized by X-ray crystal structure analyses. In solution the La_2Na_2 complex **3**-La eliminates NaC_5HR_4 (R = $CHMe_2$) to form a mixture of **2**-La and $[(C_5HR_4)La\{N(SiMe_3)_2\}_2]$ (**4**). With less a bulky bis(dimethylsilyl)amide **1**-La yields the substitution product $[(C_5HR_4)_2LaN(SiHMe_2)_2]$ (**5**) (R = $CHMe_2$).

Introduction

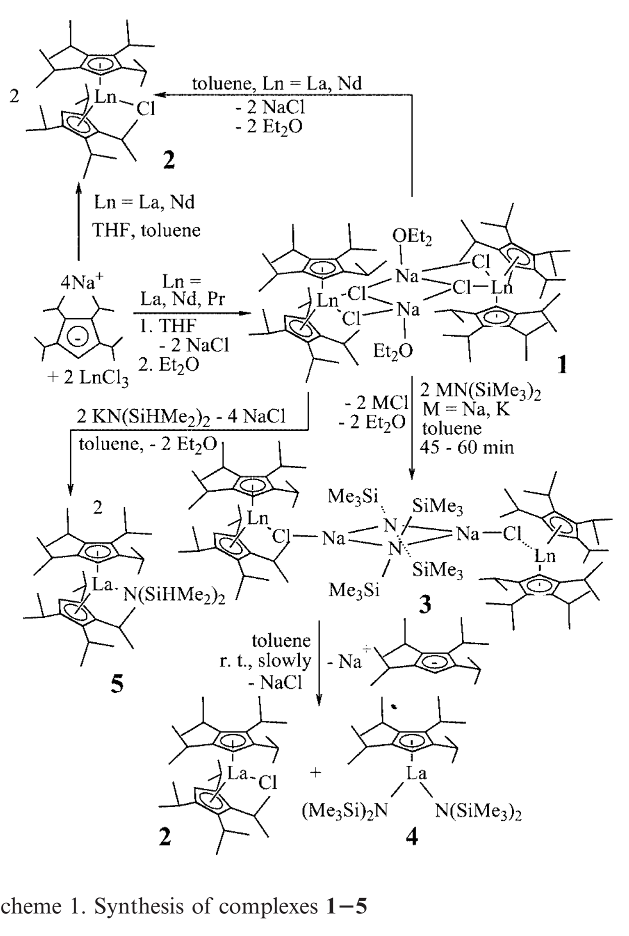
Organometallic complexes of the early lanthanides still present a challenge because of the large ionic radii of these elements.[1] The intriguing catalytic properties of cyclopentadienyl complexes of the lanthanides in a variety of C−C, C−H, or C−N bond-formation reactions[2] warrant an investigation of the impact of extremely bulky alkylcyclopentadienyl ligands on these big cations.

The tetraisopropylcyclopentadienyl ligand[3] should be bulky enough to solve problems related to donor solvent or alkali metal salt coordination even for the early lanthanides. We therefore synthesized (chloro)bis(tetraisopropylcyclopentadienyl) complexes of lanthanum, neodymium,[4] and praseodymium (this work) as starting compounds for nucleophilic substitution.

In this paper we report on the behavior of these chloro complexes in nonpolar solvents like toluene, and their reactions with $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, and $KN(SiHMe_2)_2$.

Results and Discussion

In toluene solution the (chloro)bis(tetraisopropylcyclopentadienyl)lanthanum, -praseodymium, or -neodymium sodium chloride complex $[\{(C_5HR_4)_2Ln(\mu\text{-}Cl)(\mu_3\text{-}Cl)Na(OEt_2)\}_2]$ (**1**) (R = $CHMe_2$; Ln = La, Pr, Nd: **1**-La, **1**-Pr, **1**-Nd) (Scheme 1) eliminates sodium chloride with formation of monomeric $[(C_5HR_4)_2LnCl]$ (**2**: Ln = La, Nd; R = $CHMe_2$). **2**-Nd is the first crystallographically characterized example of a solvent-free, monomeric bis(cyclopentadienyl) halo complex of the lanthanides.



Scheme 1. Synthesis of complexes **1−5**

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The crystal structure of **2**-Nd (Figure 1, Table 1) shows Nd−C distances within a narrow range from 2.71 to 2.81 Å and an angle of 133.6° between the two ring planes. Two contacts to methyl groups of the ring substituents (C12 and its symmetry-equivalent atom are at an Nd···C distance of 3.32 Å) stabilize the unusually low coordination number of the central atom. The angle C12−Nd−C12′ is 179° and forms a T-shaped arrangement with the Nd−Cl vector located on the crystallographic C_2 axis. Three out of four isopropyl α-carbon atoms are bent out of the ring plane away from the metal center by 0.1−0.3 Å, but the α-carbon atom C11 carrying the methyl C12 atom is bent towards the central atom by 0.02 Å. The isopropyl substituent at C1 of the cyclopentadienyl ring seems to adopt the role of a side chain capable of an additional stabilizing interaction. The tetraisopropylcyclopentadienyl ring in **2**-Nd thus resembles the donor-functionalized cyclopentadienyl ligands in monomeric [(2-methoxyethyl-1-indenyl)$_2$NdCl][5] or [(Me$_2$NCH$_2$CH$_2$C$_5$H$_4$)$_2$NdCl].[6] Similar intramolecular Ln···CH$_3$ interactions have been found for 1,1′,3,3′-tetra(*tert*-butyl)ytterbocene.[7]

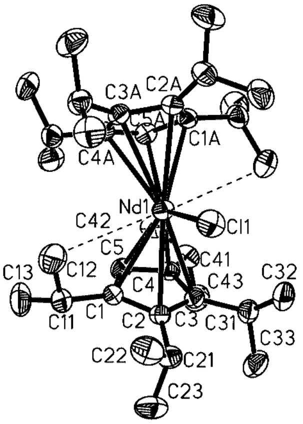

Figure 1. Crystal structure of **2**-Nd; selected bond lengths [Å] and angles [°]: Nd1−Cl1 2.713(1), Nd1−C1 2.724(4), Nd1−C2 2.801(4), Nd1−C3 2.811(4), Nd1−C4 2.782(4), Nd1−C5 2.709(4), Nd1···C12 3.318, Nd1−Cp$_{cent.}$ 2.489, Cp$_{cent.}$−Nd1−Cp$_{cent.}$ 137.3, C12···Nd1···C12a 178.7, Cl1−Nd···C12 90.6; thermal ellipsoids are at the 50% probability level

In toluene solution the (chloro)bis(tetraisopropylcyclopentadienyl)lanthanum, -praseodymium, or -neodymium sodium chloride complexes [{(C$_5$HR$_4$)$_2$Ln}$_2$(μ-Cl)$_2$(μ$_3$-Cl)$_2${Na(OEt$_2$)}$_2$] (**1**-La, **1**-Pr, **1**-Nd) react with sodium bis(trimethylsilyl)amide with formation of the tetranuclear complexes [{(C$_5$HR$_4$)$_2$Ln(μ-Cl)Na(μ-N(SiMe$_3$)$_2$]}$_2$] (**3**), which can be isolated in good yield (Scheme 1) if the reaction is stopped by solvent removal after 45−60 min. If stirring is continued for several hours, reduced yields or oily mixtures of **3** with two follow-up products are obtained. (This clean follow-up reaction of **3** will be discussed shortly.) In the solid state **3** can be stored for months at ambient temperature without noticeable decomposition.

Crystals of **3**-La, **3**-Pr, and **3**-Nd are isotypic and have been crystallographically characterized. Because of the close similarity of the structural parameters only **3**-Nd will be discussed here.

Table 1. Crystal structure determination of complexes **2**-Nd, **3**-La, **3**-Pr, and **3**-Nd

	2-Nd	**3**-La	**3**-Pr	**3**-Nd
Empirical formula	$C_{34}H_{58}ClNd$	$C_{40}H_{76}ClLaNNaSi_2$	$C_{40}H_{76}ClNNaPrSi_2$	$C_{40}H_{76}ClNNaNdSi_2$
F_w [g·mol^{-1}]	646.534	824.583	826.583	829.913
Crystal size [mm]	0.47 × 0.28 × 0.13	0.38 × 0.27 × 0.23	0.32 × 0.25 × 0.21	0.52 × 0.38 × 0.18
Space	*C*2/*c* (no. 15)	*I*2/*a* (no. 15)	*I*2/*a* (no. 15)	*I*2/*a* (no. 15)
Lattice parameters				
a [Å]	15.4470(15)	23.170(2)	23.365(2)	23.334(7)
b [Å]	12.5006(14)	17.1222(16)	17.0376(17)	17.145(4)
c [Å]	17.7273(15)	23.7779(16)	23.8476(18)	23.849(6)
β [°]	98.675(11)	102.160(9)	102.389(9)	102.53(3)
V [Å^3]	3383.9(6)	9221.5(13)	9272.2(14)	9313(4)
Z	4	8	8	8
T [K])	293(2)	293(2)	293(2)	293(2)
$D_{calcd.}$ [g·cm^{-3}]	1.269	1.196	1.181	1.179
μ [cm^{-1}9	16.32	12.70	10.65	11.89
Transmission factors	0.486−0.835	0.7124−0.8782	0.52423−0.61912	0.64602−0.74964
Θ limits [°]	2.98−24.03	2.76−25.68	2.75−25.68	2.75−25.68
Total reflections	18004	64670	64290	64551
Unique reflections	2636	8394	8628	8349
Structure solution	Direct methods	Direct methods	Direct methods	Direct methods
Program used	SIR97	SIR97	SHELXS-97	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Data/restraints/parameters	2386/0/172	6452/0/429	6697/0/599	6506/0/429
*R*1	0.0339 [$I > 2\sigma(I)$]	0.0317 [$I > 2\sigma(I)$]	0.0278 [$I > 2\sigma(I)$]	0.0348 [$I > 2\sigma(I)$]
*wR*2 (all data)	0.0926	0.0808	0.0693	0.1019
GooF (all data)	1.050	0.942	0.976	0.975
Max./min difference peak [e·Å^{-3}]	−0.842/1.345	−0.614/0.865	−0.564/0.436	−0.483/0.546

The crystal structure of **3**-Nd (Figure 2, Table 1) shows a four-membered Na_2N_2 ring with one molecule of $[(C_5HR_4)_2NdCl]$ coordinated to each of the two sodium ions via a bridging chloro ligand (Figure 2). The Nd−Cl bond length is 2.683(1) Å in **3**-Nd and the angle between the ring planes is 137.7°. The Na−Cl distance [2.767(2) Å] is shorter than that found in crystalline sodium chloride (2.82 Å).[8] The distance Nd1···C82a is 3.37 Å, and three Nd1···C distances between 3.67 and 3.94 Å are also observed for **3**-Nd. The two NSi_2 planes are not parallel, but twisted by 37.5° relative to each other. Short Na···Si distances [3.216(2)/3.172(2) Å for Si1···Na1 and Si···Na1′] and additional Na···methyl interactions (3.023/2.915 Å for Na···C17 and Na1′···C29) are obviously the reason for this distortion. Similar Na···C distances have been found for the cyclic trimer $[NaN(SiMe_3)_2]_3$ [9] and for the sodate $Na[Na\{N(SiMe_3)_2AlMe_3\}_2]$.[10] Because of this methyl-C···Na interaction in **2**-Nd one of the three N−Si−C angles at Si1 (114.8°, 114.5°, 110.7°) or Si2 (114.8°, 114.9°, 111.1°) is significantly smaller than the others. Moreover, this interaction is strong enough to stop the silyl group rotation even in solution, as can be concluded from ^1H and ^{13}C NMR spectra of **3**-La, whose crystal structure shows similar methyl C···Na distances (3.019 and 2.912 Å).

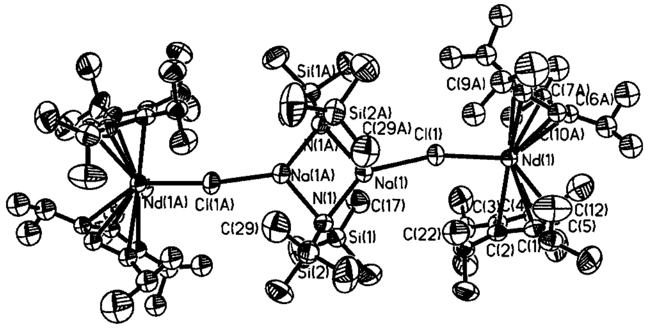

Figure 2. Crystal structure of **3**-Nd. Selected bond lengths [Å] and angles [°]: Nd1−Cl1 2.6832(9), Nd1−C1 2.757(3), Nd1−C2 2.754(3), Nd1−C3 2.766(3), Nd1−C4 2.765(3), Nd1−C5 2.720(3), Nd1−C6a 2.742(7), Nd1−C7a 2.737(7), Nd1−C8a 2.685(8), Nd1−C9a 2.709(7), Nd1−C10a 2.698(7), Nd1−$Cp_{cent.}$ 2.432, Na1···Si1 3.225, Na1···Si2a 3.172, Na1···C29a 2.912, Na1···C17 3.019, Nd1···C82a 3.372, Nd1···C62a 3.673, Nd1···C12 3.759, Nd1···C22 3.938, Cl1−Na1 2.767(2), Na1−N1 2.414(3), Na1−N1a 2.404(3), N1−Si1 1.685(3), N1−Si2 1.689(3), $Cp_{cent.}$−Nd1−$Cp_{cent.}$ 139.4, Nd1−Cl1−Na1 157.04(6), N1−Na1−N1a 101.0(2), Na1−N1−Na1a 78.38(10) thermal ellipsoids are at the 50% probability level

The NMR spectra of **3**-La are well resolved and show one set of resonances for the tetraisopropylcyclopentadienyl ring (cf. ref.[3a] for spectral pattern of C_5HR_4) and two sharp singlets at $\delta = 0.30$ and 0.34 ppm in a 1:2 ratio for the four trimethylsilyl groups. In the ^{13}C NMR spectra two $SiCH_3$ signals, with an intensity ratio of 1:2, are observed for **3**-La at $\delta = 5.3$ and 7.0 ppm. NMR spectroscopy at elevated temperatures in order to observe coalescence of the two $SiCH_3$ signals and to determine the activation barrier for $SiMe_3$ rotation was unsuccessful because **3**-La undergoes a clean follow-up reaction with deposition of 1 equiv. of sodium tetraisopropylcyclopentadienide per dimer **3** and formation of two complexes in a 1:1 ratio. One of these complexes is **2**-La, which could be identified by ^1H and ^{13}C NMR spectroscopy. The second component, according to the intensity of its NMR signals, contains only one tetraisopropylcyclopentadienyl and two bis(trimethylsilyl)amide ligands according to the formula $[(C_5HR_4)La\{N(SiMe_3)_2\}_2]$ (**4**-La). The observation of only one $SiCH_3$ signal of **4**-La arising from the clean decomposition of **3**-La supports the assignment stated above and rules out the possibility of an unknown impurity causing the 2:1 $SiCH_3$ signal pattern found for **3**-La.

In an attempt to generate a possible potassium compound analogous to **3**-Pr, potassium bis(trimethylsilyl)amide was treated with **1**-Pr instead of the sodium salt. Instead of a potassium derivative the sodium compound **3**-Pr was obtained in good yield as before. Under the conditions employed in this work the Ln_2Na_2 complexes **1** are probably not cleaved into fragments of lower nuclearity during the reaction with sodium or potassium bis(trimethylsilyl)amides. The first step could be replacement of the diethyl ether ligand coordinated to each of the sodium cations of **1** with bis(trimethylsilyl)amide anions. Elimination of alkali chloride and rearrangement then furnishes **3** as the isolable product. The attempted rare earth amide formation, a well-known reaction in lanthanide chemistry,[11] has apparently been stopped for steric reasons, and **3** can be regarded as an intermediate in the nucleophilic substitution of chloride by bis(trimethylsilyl)amide.

The composition and geometry of **3** suggests the possible formation of **3** by addition of **2** as a sort of complex ligand to sodium bis(trimethylsilyl)amide. In deuteriobenzene this reaction of **2**-La failed in our hands, however.

Since the bis(trimethylsilyl)amide ligand is obviously too bulky for nucleophilic substitution of the chloro ligand in complexes **1**, we reduced the steric bulk of the nucleophile and used potassium bis(dimethylsilyl)amide for a reaction with **1**-La. The dimer **1**-La reacts with 2 equiv. of $KN(SiHMe_2)_2$ in toluene at room temperature to form the monomeric substitution product $[(C_5HR_4)_2LaN(SiHMe_2)_2]$ (**5**) in good yield (Scheme 1).

The ^1H NMR spectra of **5** show the signals of two tetraisopropylcyclopentadienyl ligands, one doublet corresponding to the 12 methyl protons of two dimethylsilyl groups and one signal for the two Si*H* protons, which are coupled to the six protons of two adjacent methyl groups and to the lanthanum central atom. The coupling partner of each signal has been assigned by $^1H,\{^1H\}$-COSY NMR spectroscopy. The spectroscopic features of the amide ligand of **5** resemble those observed very recently for the bis(dimethylsilyl)amido ligand of *ansa*-metallocene derivatives of lanthanum. Complex **5** shows a $^1J_{Si,H}$ coupling constant of 157 Hz, close to the value of 150 Hz found for $[Me_2Si(C_5Me_4)_2LaN(SiHMe_2)_2]$ indicating a β-agostic interaction of the Si−H bond with the central atom.[12]

Conclusion

The sodium chloride adducts [{(C_5HR_4)$_2$Ln(μ-Cl)(μ$_3$-Cl)Na(OEt_2)}$_2$] (**1**) (R = $CHMe_2$, Ln = La, Pr, Nd) undergo facile diethyl ether and sodium chloride elimination in nonpolar solvents. [(C_5HR_4)$_2$NdCl] (R = $CHMe_2$) (**2**-Nd) is the first crystallographically characterized bis(cyclopentadienyl)lanthanide halo complex, which crystallizes as a monomeric molecule without additional salt or heteroatom coordination. The tetraisopropylcyclopentadienyl ligand in this example provides not only steric saturation, but also offers electronic stabilization.

With bis(trimethylsilyl)amides the sodium site is attacked rather than the lanthanide cation of complexes **1** because the large cyclopentadienyl ligands around the lanthanide cation prevent the approach of this bulky nucleophile. The complex [{(C_5HR_4)$_2$Ln(μ-Cl)(Na)μ-N($SiMe_3$)$_2$}$_2$] (**3**) resembles a reactive intermediate of the nucleophilic substitution in nonpolar solvents as it consists of the "nucleophile" [a dimeric sodium bis(trimethylsilyl)amide core] coordinated to its designated reaction partner {a neutral [(C_5HR_4)$_2$LnCl] complex}. Two sodium chloride ion-pairs serve as a spacer between the [(C_5HR_4)$_2$Ln]$^+$ cations and the [N($SiMe_3$)$_2$]$^-$ anions and steric bulk prevents salt elimination and formation of the anticipated substitution product. Instead of chloride substitution slow elimination of sodium tetraisopropylcyclopentadienide occurs and a mixture of **2** and **4** is formed. The driving force for this reaction appears to be the formation of the two Ln−N bonds of [(C_5HR_4)Ln{N($SiMe_3$)$_2$}$_2$] (**4**) along with elimination of 1 equiv. of sodium chloride during this step.

With the less bulky bis(dimethylsilyl)amide the substitution reaction proceeds as usual to furnish [(C_5HR_4)$_2$LnN($SiHMe_2$)$_2$] (**5**).

Experimental Section

General: All synthetic operations were performed under dry nitrogen in a glove box (MBraun). Tetrahydrofuran, hexane, and petroleum ether (boiling range 40−60 °C) were distilled from potassium metal, heptane and toluene from sodium metal, and pentane from a sodium/potassium alloy. NMR spectra were recorded with a Bruker AC 200 spectrometer. Chemical shifts are given in ppm and refer to the appropriate solvent signals. Mass spectra were recorded with a Finnigan MAT 90 mass spectrometer. Elemental analyses were performed with a Perkin−Elmer Elemental Analyzer 240 or 400. **1**-La, **1**-Nd[4] and sodium tetraisopropylcyclopentadienide[3d] were prepared according to published procedures.

1-Pr: A suspension of $PrCl_3$ (1.900 g, 7.6 mmol) in THF (100 mL) was stirred at ambient temperature for 30 min, then a solution of sodium tetraisopropylcyclopentadienide (4.040 g, 15.7 mmol) in THF (50 mL) was added dropwise. The mixture was stirred at room temperature for 1 h and then at reflux temperature for 13 h. The solvent was removed in vacuo and the remaining solid was extracted with two 30-mL portions of diethyl ether. After centrifugation, the orange-yellow diethyl ether extract was concentrated and stored at −35 °C to yield 2.394 g (3.1 mmol, 41%) of yellow platelets of **1**-Pr. $C_{38}H_{68}Cl_2NaOPr$ (775.77): calcd. C 58.83, H 8.83; found C 58.50, H 9.12. MS (70 eV, EI): *m*/*z* (%) = 642.0 (6.7) [(C_5HR_4)$_2$PrCl]$^+$, 607.1 (2.5) [(C_5HR_4)$_2$Pr]$^+$, 408.9 (100) [(C_5HR_4)PrCl]$^+$.

2-La: A solution of sodium tetraisopropylcyclopentadienide (0.512 g, 2 mmol) in tetrahydrofuran (10 mL) was added to $LaCl_3(THF)_2$ (0.390 g, 1.0 mmol) in 10 mL of tetrahydrofuran and the mixture stirred at 70 °C for 2 d. Removal of the solvent in vacuo, extraction of the residue with two 25-mL portions of hexane/toluene (3:1), centrifugation, and concentration left a foam, which slowly solidified upon storage under inert gas at ambient temperature to yield 0.280 g (0.44 mmol, 44%) of **2**-La. $C_{34}H_{58}ClLa$ (641.20): calcd. C 63.69, H 9.12; found C 60.04, H 8.16. ^1H NMR (200 MHz, 298 K, C_6D_6): δ = 6.18 (s, 2 H, ring-C*H*), 3.34 ("sept", 4 H, C*H*Me$_2$), 3.08 ("sept", 4 H, C*H*Me$_2$), 1.51 (d, $^3J_{H,H}$ = 7.2 Hz, 12 H, C*H*$_3$), 1.39 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, C*H*$_3$), 1.24 (d, $^3J_{H,H}$ = 7.2 Hz, 12 H, C*H*$_3$), 1.08 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, C*H*$_3$) ppm. ^{13}C NMR (50 MHz, 298 K, C_6D_6): δ = 135.5 (s, 8 C, ring-*C*CHMe$_2$), 135.0 (s, 4 C, ring-*C*CHMe$_2$), 134.5 (s, 4 C, ring-*C*CHMe$_2$), 106.1 (d, $^1J_{C,H}$ = 160 Hz, 4 C, ring-*C*H), 27.44 (d, 8 C, *C*HMe$_2$, *), 27.42 (d, 4 C, *C*HMe$_2$, *), 26.4 (q, 4 C, *C*H$_3$, *), 25.0 (q, 4 C, *C*H$_3$, *), 23.6 (q, 4 C, *C*H$_3$, *), 23.3 (q, 4 C, *C*H$_3$, *) ppm. *: Coupling constants not resolved because of signal superimposition.

2-Nd: A suspension of **1**-Nd (1.878 g, 1.2 mmol) in toluene (10 mL) was stirred at −35 °C for 1 h and at 0 °C for 17 h, then the solvents were evaporated to dryness. The green, foam-like solid was extracted with pentane (15 mL), subjected to centrifugation and concentrated to about 3 mL. Storage at −35 °C gave a green, crystalline precipitate within two weeks. A fraction of well-shaped, blue-green crystals suitable for X-ray crystallography was obtained when the mother liquor was allowed to slowly concentrate at room temperature. Combined yield 1.107 g (1.7 mmol, 71%). $C_{34}H_{58}ClNd$ (646.16): calcd. C 63.16, H 9.04; found C 62.29, H 9.02.

3-La: A solution of sodium bis(trimethylsilyl)amide (0.120 g, 0.65 mmol) in toluene (10 mL) was added to a magnetically stirred suspension of **1**-La (0.501 g, 0.32 mmol) in toluene (12 mL). Stirring was continued for 45 min, then a small amount of a gelatinous residue was separated by centrifugation and the solvents were evaporated to yield a faintly yellow, crystalline solid. The solid product was extracted with hexanes (10 mL) and traces of a colorless precipitate were removed by centrifugation. Drying in vacuo yielded 0.372 g (0.23 mmol, 70%) of faintly yellow, crystalline product. $C_{80}H_{152}Cl_2N_2Na_2La_2Si_4$ (1649.16): calcd. C 59.27, H 9.45, N 1.73; found C 57.32, H 8.81, N 1.55. ^1H NMR (200 MHz, 298 K, C_6D_6): δ = 6.18 (s, 2 H, ring-C*H*), 3.34 (sept, 8 H, C*H*Me$_2$), 3.05 (sept, 8 H, C*H*Me$_2$), 1.50 (d, $^3J_{H,H}$ = 7.3 Hz, 24 H, C*H*$_3$), 1.38 (d, $^3J_{H,H}$ = 6.8 Hz, 24 H, C*H*$_3$), 1.25 (d, $^3J_{H,H}$ = 7.1 Hz, 24 H, C*H*$_3$), 1.07 (d, $^3J_{H,H}$ = 6.6 Hz, 24 H, C*H*$_3$), 0.34 (s, 24 H, SiC*H*$_3$), 0.30 (s, 12 H, SiC*H*$_3$) ppm. ^{13}C NMR (50 MHz, 298 K, C_6D_6): δ = 135.5 (s, 8 C, ring-*C*CHMe$_2$), 134.7(s, 8 C, ring-*C*CHMe$_2$), 106.4 (d, $^1J_{C,H}$ = 160 Hz, 4 C, ring-*C*H), 27.44 (d, 8 C, *C*HMe$_2$, *), 27.42 (d, 8 C, *C*HMe$_2$, *), 26.5 (q, 8 C, *C*H$_3$, *), 25.0 (q, 8 C, *C*H$_3$, *), 23.6 (q, 8 C, *C*H$_3$, *), 23.3 (q, 8 C, *C*H$_3$, *), 7.0 (q, $^1J_{C,H}$ = 116 Hz, 8 C, Si*C*H$_3$), 5.3 (q, $^1J_{C,H}$ = 117 Hz, 4 C, Si*C*H$_3$) ppm. *: Coupling constants not resolved because of signal superimposition. MS (70 eV, EI): *m*/*z* (%) = 639.3 (5) [(C_5HR_4)$_2$LaCl]$^+$, 604.4 (9) [(C_5HR_4)$_2$La]$^+$, 531.4 (29) [(C_5HR_4)LaN($SiMe_3$)$_2$]$^+$, 458.5 (36) [(C_5HR_4)$_2$LaNSiMe$_3$]$^+$, 406.5 (79) [(C_5HR_4)LaCl]$^+$, 233.9 (24) [$C_5H_2R_4$]$^+$, 145.9 (100) [Si_2Me_6]$^+$.

3-Nd: A solution of sodium bis(trimethylsilyl)amide (0.122 g, 0.66 mmol) in toluene (5 mL) was added to a magnetically stirred suspension of **1**-Nd (0.513 g, 0.33 mmol) in toluene (20 mL). The suspended material dissolved initially, but after about 40 min a barely visible turbidity was observed. Stirring was discontinued after 45 min, then a small amount of a sticky residue was separated by centrifugation. The solvents were evaporated and the solid product was washed with hexanes (15 mL). Drying in vacuo yielded 0.375 g (0.23 mmol, 69%) green, microcrystalline solid. The green hexane washings produced green crystals on slow concentration. $C_{80}H_{152}Cl_2N_2Na_2Nd_2Si_4$ (1659.82): calcd. C 57.89, H 9.23, N 1.69; found C 57.78, H 9.31, N 1.56. MS (70 eV, EI): *m/z* (%) = 609.2 (5) $[(C_5HR_4)_2Nd]^+$, 412.0 (11) $[(C_5HR_4)NdCl]^+$, 234.2 (84) $[C_5H_2R_4]^+$, 191.1 (100) $[C_{14}H_{22}]^+$, 146.0 (91) $[Si_2Me_6]^+$.

3-Pr: From **1**-Pr (0.500 g; 0.31 mmol) and $KN(SiMe_3)_2$ (0.130 g; 0.65 mmol), 0.390 g (0.24 mmol, 77%) of the light yellow, crystalline praseodymium complex were obtained by the same procedure. Single crystals were grown from hexane at room temperature by slow concentration. $C_{80}H_{152}Cl_2N_2Na_2Pr_2Si_4$ (1653.16): calcd. C 58.12, H 9.27, N 1.69; found C 58.06, H, 9.05, N 1.68.

4-La as a 1:1 Mixture with 2-La: A solution of sodium bis(trimethylsilyl)amide (0.118 g, 0.64 mmol) in toluene (3 mL) was added slowly to a solution of **1**-La (0.504 g, 0.32 mmol) in toluene (15 mL) at room temperature. The mixture was stirred at room temperature for 12 h. Centrifugation and evaporation of the solvents gave 0.320 g of an oily mixture of equivalent amounts of **2**-La and **4**-La (75%), which could not be separated. ^1H NMR for **4**-La (200 MHz, 298 K, C_6D_6): δ = 6.07 (s, 1 H, ring-C*H*), 3.08 ("sept", 4 H, C*H*Me$_2$), 1.50 (d, $^3J_{H,H}$ = 7.3 Hz, 6 H, CH_3), 1.49 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH_3), 1.23 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 1.14 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CH_3), 0.30 (s, 36 H, SiCH_3) ppm. ^{13}C NMR (50 MHz, 298 K, C_6D_6): δ = 136.6 (s, 2 C, ring-*C*CHMe$_2$), 133.0 (s, 2 C, ring-*C*CHMe$_2$), 108.7 (d, $^1J_{C,H}$ = 159 Hz, 1 C, ring-*C*H), 27.6 (d, 2 C, *C*HMe$_2$, *), 27.1 (q, 2 C, *C*H$_3$, *), 27.0 (d, 2 C, *C*HMe$_2$, *), 25.3 (q, 2 C, *C*H$_3$, *), 25.0 (q, 2 C, *C*H$_3$, *), 24.6 (q, 2 C, *C*H$_3$, *), 5.3 (q, $^1J_{C,H}$ = 117 Hz, 12 C, Si*C*H$_3$) ppm. *: Coupling constants not resolved because of signal superimposition.

5-La: At room temperature a solution of $KN(SiHMe_2)_2$ (0.077 g; 0.45 mmol) in toluene (4 mL) was added dropwise with stirring to a solution of **1**-La (0.351 g; 0.225 mmol) in toluene (5 mL). A white precipitate formed and stirring was continued for 36 h. After centrifugation, the solvents were evaporated to dryness yielding an off-white, crystalline residue, which was redissolved in hexane (3 mL). Evaporation of the solvent, extraction with pentane (3 mL) and slow concentration of the solution gave 0.221 g (0.30 mmol, 67%) of faintly yellow crystals. $C_{38}H_{72}NLaSi_2$ (730.08): calcd. C 61.84, H 9.83, N 1.90; found C 60.17, H 9.90, N 1.86. ^1H NMR (200 MHz, 298 K, C_6D_6): δ = 6.33 (s, 2 H, ring-C*H*), 4.57 (m, $^1J_{Si,H}$ = 157 Hz, 2 H, Si*H*Me$_2$) 3.27 ("sept", 4 H, C*H*Me$_2$), 3.15 ("sept", 4 H, C*H*Me$_2$), 1.51 (d, $^3J_{H,H}$ = 7.2 Hz, 12 H, CH_3), 1.50 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3), 1.28 (d, $^3J_{H,H}$ = 7.0 Hz, 12 H, CH_3), 1.18 (d, $^3J_{H,H}$ = 6.7 Hz, 24 H, CH_3), 0.40 (d, $^3J_{H,H}$ = 2.8 Hz, 12 H, SiCH_3) ppm. ^{13}C NMR (50 MHz, 298 K, C_6D_6): δ = 133.3 (s, 4 C, ring-*C*CHMe$_2$), 133.2 (s, 4 C, ring-*C*CHMe$_2$), 106.6 (d, $^1J_{C,H}$ = 159 Hz, 2 C, ring-*C*H), 27.8 (d, 4 C, *C*HMe$_2$, *), 27.3 (d, 4 C, *C*HMe$_2$, *), 26.9 (q, 4 C, *C*H$_3$, *), 25.4 (q, 4 C, *C*H$_3$, *), 24.8 (q, 4 C, *C*H$_3$, *), 24.1 (q, 4 C, *C*H$_3$, *), 4.3 (q, $^1J_{C,H}$ = 118 Hz, 4 C, Si*C*H$_3$) ppm. * Coupling constants not determined due to signal superimposition, assignment confirmed by DEPT experiments.

X-ray Crystallography: Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171977 (**2**-Nd), -171978 (**3**-Nd), -171979 (**3**-Pr) amd -171980 (**3**-La). Copies of the data can be obtained free of charge on applicaton to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. A Stoe IPDS and Mo-K_α radiation were used for all structure determinations reported here.

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