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Synthesis and Structural Characterization of Novel Organolanthanide Clusters Containing Amido and Imido Groups

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Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with 4 equiv of $NaNH_2$ in THF, followed by reaction with 1 equiv of $LnCl_3$ at room temperature, afforded $[\{(\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Ln\}_2(\mu_3\text{-Cl})(THF)]_2(\mu_4\text{-NH})\cdot nOC_4H_8$ ($n = 1$, Ln = Gd (**Ia**), Er (**Ib**); $n = 0$, Ln = Dy (**Ic**)), which represent not only the first examples of organometallic clusters containing a central μ_4-imido group but also the first organolanthanide indenyl clusters to be reported. Another type of tetranuclear cluster, $[\{(\eta^5\text{-}C_9H_6SiMe_2)_2N\}(\mu_2\text{-}NH_2)Ln_2(THF)_2]_2(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_2\cdot THF$ (Ln = Gd (**IIa**), Y (**IIb**)), was obtained if the above reactions were carried out at reflux temperature. This type of cluster can also be prepared by refluxing cluster type **I** in THF in the presence of NaCl. Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with 8 equiv of $NaNH_2$ in THF, followed by reaction with 1 equiv of $LnCl_3$ at room temperature, gave the trinuclear clusters $[(\eta^5\text{-}C_9H_6\text{-}SiMe_2)_2N][\mu_2,\mu_2\text{-}Me_2Si(NH)_2](\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)(\mu_2\text{-Cl})_2Ln_3(THF)_3$ (Ln = Gd (**IIIa**), Er (**IIIb**)). These results indicate that $NaNH_2$ serves as both base and nucleophile in the reactions. The *o*-carborane can be recovered by sublimation under vacuum. The structures of all tetra- and trinuclear clusters were confirmed by single-crystal X-ray analyses.

Introduction

Imido−transition-metal complexes play an important role both in biological processes such as nitrogen fixation and in a series of industrial processes.[1] Cycloadditions, C−H bond activations, and ring-opening polymerizations can all be catalyzed by various imido complexes.[1−3] Numerous imido−metal complexes have been reported;[1−4] however, syntheses of organometallic clusters containing a central μ_4-imido group have thus far remained elusive.

In comparison with d-block transition-metal complexes, the imido− or amido−lanthanide complexes have been much less studied, and examples of organolanthanide clusters containing imido or amido groups are even rare.[5] We have recently communicated the obtainment of a novel organometallic cluster bearing a μ_4-NH^{2-} group that was derived from an unexpected reaction between $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ and excess $NaNH_2$.[6] Encouraged by this exciting result, we have explored these reactions and report herein the syntheses and structural characterization of three types of novel organolanthanide clusters containing imido or amido groups. The possible pathways of the formation of these clusters are also discussed.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous $LnCl_3$ was prepared from the hydrates by standard procedures.[7] $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ was prepared according to the procedures previously described.[8] All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvent or with respect to internal or external TMS (0.00 ppm) for proton and carbon chemical shifts and to external $BF_3\cdot OEt_2$ (0.00 ppm) for boron chemical shifts. Elemental analyses were performed by MEDAC Ltd, Brunel University, Middlesex, U.K.

Preparation of $[\{(\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Gd\}_2(\mu_3\text{-Cl})(THF)]_2(\mu_4\text{-NH})\cdot OC_4H_8$ (Ia). To a suspension of $NaNH_2$ (0.16 g, 4.1 mmol) in THF (10 mL) was added a THF solution (5 mL) of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and the mixture was stirred at room temperature for 20 h. The resulting purple solution was filtered into a stirred suspension

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of $GdCl_3$ (0.26 g, 1.0 mmol) in THF (8 mL) at room temperature, and this reaction mixture was then stirred overnight. After filtration, the clear purple solution was concentrated to about 8 mL; *n*-hexane vapor diffusion resulted in the production of **Ia** as colorless crystals over days (0.21 g, 51% based on $GdCl_3$). ^1H NMR (pyridine-d_5): many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3267 (w), 3057 (w), 2954 (s), 2884 (s), 1448 (m), 1406 (m), 1329 (m), 1243 (s), 1007 (vs), 870 (m), 839 (s), 777 (s), 712 (m), 665 (m). Anal. Calcd for $C_{50}H_{65}Cl_2Gd_4N_5O_{1.5}Si_4$ (**Ia**$-$1.5THF): C, 38.19; H, 4.17; N, 4.45. Found: C, 37.82; H, 4.30; N, 4.25. *o*-$C_2B_{10}H_{12}$ can be recovered in 71% yield by sublimation of the residue under vacuum.

Preparation of [{(η^5-μ_2-$C_9H_6SiMe_2NH$)Er}$_2$(μ_3-Cl)(THF)]$_2$(μ_4-NH)·OC_4H_8 (Ib). This compound was prepared as light pink crystals from $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), $NaNH_2$ (0.16 g, 4.1 mmol), and $ErCl_3$ (0.27 g, 1.0 mmol) in 35 mL of THF using the procedures described above for **Ia**: yield 0.23 g (49% based on $ErCl_3$). ^1H NMR (pyridine-d_5): δ 7.23 ($\nu_{1/2}$ = 15 Hz), 7.05 ($\nu_{1/2}$ = 15 Hz), 6.67 ($\nu_{1/2}$ = 17 Hz), 6.23 ($\nu_{1/2}$ = 17 Hz), 3.04 ($\nu_{1/2}$ = 30 Hz), 1.96 ($\nu_{1/2}$ = 30 Hz) (C_9H_6), 3.41 ($\nu_{1/2}$ = 10 Hz), 1.35 ($\nu_{1/2}$ = 10 Hz) (THF), 0.89 ($\nu_{1/2}$ = 15 Hz), 0.54 ($\nu_{1/2}$ = 10 Hz) (Me_2Si). IR (KBr, cm^{-1}): ν 3268 (m), 3065 (m), 2955 (s), 2892 (m), 1458 (m), 1328 (s), 1246 (s), 1143 (m), 1024 (m), 838 (vs), 813 (vs), 775 (vs), 747 (s), 662 (m), 609 (m). Anal. Calcd for $C_{56}H_{77}Cl_2Er_3N_5O_3Si_4$: C, 39.09; H, 4.51; N, 4.07. Found: C, 38.76; H, 4.92; N, 3.96.

Preparation of [{(η^5-μ_2-$C_9H_6SiMe_2NH$)Dy}$_2$(μ_3-Cl)(THF)]$_2$(μ_4-NH) (Ic). This compound was prepared as colorless crystals from $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), $NaNH_2$ (0.16 g, 4.1 mmol), and $DyCl_3$ (0.27 g, 1.0 mmol) in 30 mL of THF using the procedures described above for **1a**: yield 0.17 g (41% based on $DyCl_3$). The ^1H NMR spectrum gave many broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3266 (w), 3063 (w), 2954 (m), 2891 (m), 1446 (m), 1401 (m), 1327 (m), 1247 (s), 1143 (m), 1023 (m), 872 (m), 837 (vs), 812 (vs), 772 (vs), 748 (s), 661 (m). Anal. Calcd for $C_{52}H_{69}Cl_2Dy_4N_5O_2Si_4$: C, 38.33; H, 4.26; N, 4.30. Found: C, 37.95; H, 4.03; N, 4.46.

Preparation of [{(η^5-$C_9H_6SiMe_2$)$_2$N}(μ_2-NH_2)Gd_2(THF)$_2$]$_2$(μ_3-Cl)$_2$(μ_2-Cl)$_2$·OC_4H_8 (IIa). To a suspension of $NaNH_2$ (0.16 g, 4.1 mmol) in THF (10 mL) was added a THF solution (5 mL) of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and the mixture was stirred at room temperature for 20 h. The resulting purple solution was filtered into a stirred suspension of $GdCl_3$ (0.26 g, 1.0 mmol) in THF (8 mL) at room temperature, and this reaction mixture was then refluxed overnight. After filtration, the clear purple solution was concentrated to about 8 mL; *n*-hexane vapor diffusion gave **IIa** as light brown crystals over days (0.25 g, 54% based on $GdCl_3$). The ^1H NMR spectrum gave several very broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3261 (w), 3069 (m), 2954 (s), 2888 (s), 1449 (s), 1405 (s), 1384 (s), 1240 (s), 1151 (s), 1005 (vs), 838 (s), 775 (vs), 711 (s), 668 (s). Anal. Calcd for $C_{64}H_{92}Cl_4Gd_4N_4O_5Si_4$: C, 40.87; H, 4.93; N, 2.98. Found: C, 41.32; H, 5.20; N, 2.94.

This compound can also be prepared by refluxing a mixture of **Ia** (0.07 g, 0.042 mmol) and NaCl (0.1 g, 1.71 mmol) in THF (10 mL) overnight, followed by procedures described above for **IIa**: yield 0.030 g (38%).

Preparation of [{(η^5-$C_9H_6SiMe_2$)$_2$N}(μ_2-NH_2)Y_2(THF)$_2$]$_2$(μ_3-Cl)$_2$(μ_2-Cl)$_2$·OC_4H_8 (IIb). This compound was prepared as colorless crystals from $NaNH_2$ (0.16 g, 4.1 mmol), $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and YCl_3 (0.20 g, 1.0 mmol) in THF (30 mL) using the procedures described above for **IIa**: yield 0.23 g (57% based on YCl_3). ^1H NMR (pyridine-d_5): δ 8.72 (m, 4H), 7.79 (m, 4H), 7.44 (m, 4H), 7.23 (m, 4H), 7.04 (m, 4H), 6.34 (m, 4H) (C_9H_6), 4.68 (br s, 4H) (NH_2), 3.42 (m, 20H), 1.41 (m, 20H) (OC_4H_8), 1.22 (s, 6H), 0.97 (s, 6H), 0.35 (s, 6H), 0.16 (s, 6H) (CH_3). ^{13}C NMR (pyridine-d_5): δ 133.88, 132.83, 129.85, 128.90, 127.34, 125.75, 124.99, 123.00, 122.46, 121.26, 121.01, 120.71, 120.56, 115.29, 107.33, 104.98, 104.00, 102.88 (C_9H_6), 68.18, 26.16 (OC_4H_8), 10.18, 8.88, 8.23, 4.06 (CH_3). IR (KBr, cm^{-1}): ν 3268 (w), 3073 (m), 3056 (m), 2956 (s), 2893 (m), 1447 (m), 1409 (m), 1332 (s), 1246 (s), 1155 (s), 1007 (vs), 869 (m), 839 (s), 777 (vs), 756 (s), 715 (m). Anal. Calcd for $C_{64}H_{92}Cl_4N_4O_5Si_4Y_4$: C, 47.82; H, 5.77; N, 3.49. Found: C, 47.41; H, 6.05; N, 3.14.

Preparation of [(η^5-$C_9H_6SiMe_2$)$_2$N][μ_2,μ_2-$Me_2Si(NH)_2$](η^5-μ_2-$C_9H_6SiMe_2NH$)(μ_2-Cl)$_2$$Gd_3(THF)_3$ (IIIa). To a suspension of $NaNH_2$ (0.32 g, 8.1 mmol) in THF (15 mL) was added a THF solution (5 mL) of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and the mixture was stirred at room temperature for 20 h. The resulting purple solution was filtered into a stirred suspension of $GdCl_3$ (0.26 g, 1.0 mmol) in THF (8 mL) at room temperature, and this reaction mixture was then stirred overnight. After filtration, the clear purple solution was concentrated to about 8 mL; *n*-hexane vapor diffusion resulted in **IIIa** as colorless crystals over days (0.27 g, 59% based on $GdCl_3$). The ^1H NMR spectrum gave many very broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3262 (m), 3070 (m), 2955 (s), 2890 (s), 1451 (m), 1405 (m), 1328 (s), 1241 (vs), 1148 (m), 1010 (vs), 831 (vs), 771 (vs), 756 (vs), 713 (s), 668 (m). Anal. Calcd for $C_{47}H_{69}Cl_2Gd_3N_4O_3Si_4$: C, 40.52; H, 4.99; N, 4.02. Found: C, 40.81; H, 5.25; N, 3.92.

Preparation of [(η^5-$C_9H_6SiMe_2$)$_2$N][μ_2,μ_2-$Me_2Si(NH)_2$](η^5-μ_2-$C_9H_6SiMe_2NH$)(μ_2-Cl)$_2$$Er_3(THF)_3$ (IIIb). This compound was prepared as purple crystals from $NaNH_2$ (0.32 g, 8.1 mmol), $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and $ErCl_3$ (0.27 g, 1.0 mmol) in THF (40 mL) using the procedures described above for **IIIa**: yield 0.23 g (49% based on $ErCl_3$). The ^1H NMR spectrum was complicated, consisting of extremely broad, unresolved resonances. IR (KBr, cm^{-1}): ν 3270 (m), 3059 (m), 2953 (s), 2892 (m), 1458 (m), 1404 (m), 1329 (m), 1245 (s), 1017 (vs), 837(vs), 770 (vs), 657 (m), 609 (m). Anal. Calcd for $C_{45}H_{65}Cl_2Er_3N_4O_{2.5}Si_4$ (**IIIb**$-$$^1/_2$THF): C, 38.96; H, 4.72; N, 4.04. Found: C, 38.54; H, 4.46; N, 4.40.

X-ray Structure Determination. All single crystals were immersed in Paratone-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS$-$IIC imaging plate for **Ia**,**b** and **IIa**.**b** and on a Rigaku AFC7R diffractometer for **Ic** and **IIIa**,**b** using Mo Kα radiation (λ = 0.710 73 Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program.[9] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the Siemens SHELXTL program package (PC version).[10] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1. Selected bond distances and angles are listed in Table 2. Further details are included in the Supporting Information.

Results

Synthesis and Characterization of [{(η^5-μ_2-$C_9H_6SiMe_2NH$)Ln}$_2$(μ_3-Cl)(THF)]$_2$(μ_4-NH)·*n*THF. Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with 4 equiv of $NaNH_2$ in THF at room temperature for 20 h, followed by reaction with 1 equiv of $LnCl_3$ at room temperature, after workup, afforded novel tetranuclear clusters of the general formula [{(η^5-μ_2-$C_9H_6SiMe_2NH$)Ln}$_2$(μ_3-Cl)(THF)]$_2$(μ_4-NH)·*n*THF in moderate yield (Scheme 1). These clusters are air- and moisture-sensitive. They are soluble in THF, DME, and pyridine and slightly soluble in toluene but insoluble in *n*-hexane.

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[10] SHELXTL V 5.03 Program Package; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

Table 1. Crystal Data and Summary of Data Collection and Refinement for Ia−c, IIa,b, and IIIa,b

	Ia	**Ib**	**Ic**	**IIa**	**IIb**	**IIIa**	**IIIb**
formula	$C_{56}H_{77}Cl_2Gd_4N_5O_3Si_4$	$C_{56}H_{77}Cl_2Er_4N_5O_3Si_4$	$C_{52}H_{69}Cl_2Dy_4N_5O_2Si_4$	$C_{64}H_{92}Cl_4Gd_4N_4O_5Si_4$	$C_{64}H_{92}Cl_4N_4O_5Si_4Y_4$	$C_{47}H_{69}Cl_2Gd_3N_4O_3Si_4$	$C_{47}H_{69}Cl_2Er_3N_4O_3Si_4$
cryst size (mm)	0.15 × 0.21 × 0.28	0.04 × 0.13 × 0.14	0.27 × 0.38 × 0.38	0.40 × 0.45 × 0.46	0.23 × 0.28 × 0.40	0.18 × 0.20 × 0.30	0.30 × 0.40 × 0.50
fw	1680.5	1720.5	1629.4	1880.6	1607.2	1393.1	1423.1
cryst class	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Aba*2	*Aba*2	*Aba*2	$P2_1/c$	$P2_1/c$	C2/*c*	*C*2/*c*
a, Å	21.625(2)	21.528(1)	21.645(7)	22.835(5)	22.642(5)	40.761(8)	41.198(8)
b, Å	19.226(2)	19.101(1)	19.147(5)	16.422(3)	16.475(3)	17.628(4)	17.528(4)
c, Å	15.125(1)	15.104(1)	15.088(4)	22.835(5)	22.642(5)	20.126(4)	19.891(4)
β, deg	90.00	90.00	90.00	101.70(3)	101.18(3)	113.62 3)	114.41(3)
V, Å^3	6288.4(8)	6210.9(6)	6253(3)	8385(3)	8286(3)	13249(5)	13080(5)
Z	4	4	4	4	4	8	8
D_{calcd}, Mg/m^3	1.775	1.840	1.731	1.490	1.288	1.397	1.445
radiation (λ, Å)				Mo Kα (0.710 73)			
2θ range, deg	3.0−52.0	3.0−52.0	4.0−51.0	4.0−50.0	2.0−50.0	4.0−52.0	4.0−50.0
μ, mm^{-1}	4.369	5.557	4.926	3.348	3.002	3.155	4.003
F(000)	3272	3336	3144	3696	3296	5480	5576
no. of obsd rflns	3018	2873	2844	12 007	7536	13 012	5620
no. of params refnd	328	340	308	814	812	569	568
goodness of fit	1.058	1.137	1.027	1.105	1.196	1.061	1.026
R1	0.063	0.052	0.037	0.076	0.103	0.060	0.061
wR2	0.158	0.112	0.096	0.208	0.228	0.170	0.166

Scheme 1

$$Me_2Si(C_9H_7)(C_2B_{10}H_{11}) \xrightarrow[\text{(2) LnCl}_3\text{/room temp}]{\text{(1) 4NaNH}_2\text{/THF}} [\{(\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Ln\}_2(\mu_3\text{-Cl})(THF)]_2\text{-}(\mu_4\text{-NH})\cdot n\text{THF} + [C_2B_{10}H_{11}]Na$$

$n = 1$, Ln = Gd (**Ia**), Er (**Ib**); $n = 0$, Ln = Dy (**Ic**)

The IR spectra of three clusters are quite similar, showing a characteristic N−H absorption at about 3270 cm^{-1}. No characteristic B−H absorption at about 2600 cm^{-1} was observed in the IR spectra, indicating that these clusters do not contain any carboranyl groups.[8,11,12] Due to the strong paramagnetism of Gd^{3+} ($\mu_{eff} = 8.0\ \mu_B$), Er^{3+} ($\mu_{eff} = 9.5\ \mu_B$), and Dy^{3+} ($\mu_{eff} = 10.6\ \mu_B$),[13] the ^{1}H NMR spectra are not very informative. The formulation of these clusters is based primarily on their single-crystal X-ray analyses and elemental analyses.

The solid-state structures reveal that compounds **Ia**−**c** are tetranuclear clusters and they are isostructural and isomorphous. There is one solvated THF molecule in the crystal lattices of clusters **Ia** and **Ib**, respectively. Figure 1 shows the representative structure of these three clusters. Each structure contains a butterfly arrangement of four metals which are connected by four doubly bridging μ_2-NHSiMe$_2$(indenyl) units over the edges, by two triply bridging μ_3-Cl atoms spanning Ln(1), Ln(2), Ln(2A) and Ln(1A), Ln(2), Ln(2A), respectively, and by a quadruply bridging μ_4-NH group located on the crystallographic 2-fold axis. The coordination sphere around each metal is completed by either bonding to one indenyl in a η^5-fashion or bonding to both η^5-indenyl and one THF molecule (for Ln(1) and Ln(1A)). As a result, each metal has a distorted-octahedral geometry with a formal coordination number of 8. As far as we are aware, they are the first organometallic clusters containing a central μ_4-NH group to be reported.

The N atom of the μ_4-NH group adopts a distorted-trigonal-bipyramidal geometry with Ln(1) and Ln(1A) occupying the axial sites, the Ln(1)−N(3)−Ln(1A) and Ln(2)−N(3)−Ln(2A) angles being 174.9(5) and 107.1(4)° for **Ia**, 176.3(3) and 105.1(3)° for **Ib**, and 174.2(3) and 107.3(2)° for **Ic**, respectively. The average Ln−N(3) (μ_4-NH) distances are 2.450(6) Å in **Ia**, 2.406(4) Å in **Ib**, and 2.418(3) Å in **Ic**, respectively. The differences in the above distances are in good agreement with the lanthanide contraction.[14] These measured values can be compared with the 2.350(2) Å Sm−N (μ_5-N$_2$) distance in [(THF)$_2$Li(OEPG)Sm]$_2$(μ_5-N$_2$Li$_4$) (OEPG = octaethylporphyrinogen),[15] the 2.500(9) Å Sm−N (μ_3-NHNH) distance in [(C$_5$Me$_5$)Sm]$_4$(μ_3-NHNH)$_2$(μ_2,μ-NHNH$_2$)$_4$-(NH$_3$)$_2$,[16] and the 2.24(1) Å Yb−N (μ_3-NPh) distance in Yb$_4$(μ-η^2:η^2-N$_2$Ph$_2$)$_4$(μ_3-NPh)$_2$(THF)$_4$.[17] The average Ln−N (μ_2-NHSiMe$_2$(indenyl)) distances are 2.426(7) Å in **Ia**, 2.395(4) Å in **Ib**, and 2.406(4) Å in **Ic**, respectively, which are somewhat shorter than the relevant Ln−N(3) distances, probably due to the different coordination environments of the nitrogen atoms. The average Ln−C distances of 2.751(14) Å in **Ia**, 2.704(7) Å in **Ib**, and 2.726(6) Å in **Ic** are comparable to those normally observed in indenyllanthanide compounds.[8,18] The average Ln−Cl distances are 2.852(2) Å in **Ia**, 2.790(1) Å in **1c**, and 2.838(2) Å in **1b**, respectively, which are

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Table 2. Selected Interatomic Distances (Å) and Angles (deg)

Cluster **Ia**							
Gd(1)−N(1)	2.496(7)	Gd(2)−N(1A)	2.391(7)	Gd(1)−C(11)	2.654(9)	Gd(2)−C(21)	2.639(10)
Gd(1)−N(2)	2.354(6)	Gd(2)−N(2)	2.464(6)	Gd(1)−C(12)	2.684(14)	Gd(2)−C(22)	2.668(10)
Gd(1)−N(3)	2.495(1)	Gd(2)−N(3)	2.405(6)	Gd(1)−C(13)	2.787(10)	Gd(2)−C(23)	2.787(11)
Gd(1)−Cl(1)	2.824(2)	Gd(2)−Cl(1)	2.927(2)	Gd(1)−C(18)	2.811(9)	Gd(2)−C(28)	2.724(9)
Gd(1)−O(1)	2.431(7)	Gd(2)−Cl(1A)	2.805(2)	Gd(1)−C(19)	2.902(9)	Gd(2)−C(29)	2.853(10)
Gd(2)−N(3)−Gd(1)	91.6(1)	Gd(1)−N(3)−Gd(2A)	91.5(1)	Gd(1)−N(1)−Gd(2A)	91.8(2)	Gd(1)−Cl(1)−Gd(2)	75.30(5)
Gd(1)−N(3)−Gd(1A)	174.9(5)	Gd(2)−N(3)−Gd(2A)	107.1(4)	Gd(1)−N(2)−Gd(2)	93.6(2)	Gd(1)−Cl(1)−Gd(2A)	77.13(5)
						Gd(2)−Cl(1)−Gd(2A)	84.90(6)
Cluster **Ib**							
Er(1)−N(1)	2.431(4)	Er(2)−N(1)	2.345(4)	Er(1)−C(11)	2.635(5)	Er(2)−C(21)	2.588(6)
Er(1)−N(2)	2.330(4)	Er(2)−N(2A)	2.473(4)	Er(1)−C(12)	2.684(7)	Er(2)−C(22)	2.608(6)
Er(1)−N(3)	2.425(1)	Er(2)−N(3)	2.386(4)	Er(1)−C(13)	2.825(7)	Er(2)−C(23)	2.700(7)
Er(1)−Cl(1)	2.762(1)	Er(2)−Cl(1)	2.742(1)	Er(1)−C(18)	2.753(6)	Er(2)−C(28)	2.705(7)
Er(1)−O(1)	2.337(4)	Er(2)−Cl(1A)	2.866(1)	Er(1)−C(19)	2.881(6)	Er(2)−C(29)	2.664(6)
Er(2)−N(3)−Er(2A)	105.1(3)	Er(1)−N(3)−Er(1A)	176.3(3)	Er(1)−N(1)−Er(2)	91.7(1)	Er(1)−Cl(1)−Er(2)	77.02(4)
Er(2)−N(3)−Er(1)	90.8(1)	Er(2)−N(3)−Er(1A)	91.5(1)	Er(1)−N(2)−Er(2A)	91.6(1)	Er(1)−Cl(1)−Er(2A)	75.46(3)
						Er(2)−Cl(1)−Er(2A)	84.97(4)
Cluster **Ic**							
Dy(1)−N(1)	2.486(4)	Dy(2)−N(1A)	2.350(4)	Dy(1)−C(11)	2.600(5)	Dy(2)−C(21)	2.630(5)
Dy(1)−N(2)	2.379(4)	Dy(2)−N(2)	2.408(4)	Dy(1)−C(12)	2.637(6)	Dy(2)−C(22)	2.663(6)
Dy(1)−N(3)	2.472(1)	Dy(2)−N(3)	2.364(3)	Dy(1)−C(13)	2.760(6)	Dy(2)−C(23)	2.800(6)
Dy(1)−Cl(1)	2.823(1)	Dy(2)−Cl(1)	2.783(1)	Dy(1)−C(18)	2.748(6)	Dy(2)−C(28)	2.755(5)
Dy(1)−O(1)	2.383(4)	Dy(2)−Cl(1A)	2.915(1)	Dy(1)−C(19)	2.841(6)	Dy(2)−C(29)	2.825(6)
Dy(1)−N(3)−Dy(1A)	174.2(3)	Dy(1A)−N(3)−Dy(2)	91.54(7)	Dy(2A)−N(1)−Dy(1)	91.54(14)	Dy(1)−Cl(1)−Dy(2A)	76.44(4)
Dy(1)−N(3)−Dy(2)	91.87(7)	Dy(2)−N(3)−Dy(2A)	107.3(2)	Dy(2)−N(2)−Dy(1)	93.10(14)	Dy(2)−Cl(1)−Dy(1A)	76.39(4)
						Dy(2)−Cl(1)−Dy(2A)	83.87(4)
Cluster **IIa**							
Gd(1)−O(1)	2.379(4)	Gd(2)−O(4)	2.449(5)	Gd(3)−O(2)	2.480(4)	Gd(4)−O(3)	2.357(4)
Gd(1)−N(4)	2.329(4)	Gd(2)−N(1)	2.344(4)	Gd(3)−N(2)	2.342(4)	Gd(4)−N(3)	2.336(4)
Gd(1)−Cl(2)	2.751(1)	Gd(2)−N(4)	2.435(4)	Gd(3)−N(3)	2.403(4)	Gd(4)−Cl(2)	2.732(2)
Gd(1)−Cl(3)	2.764(1)	Gd(2)−Cl(1)	2.807(1)	Gd(3)−Cl(1)	2.805(2)	Gd(4)−Cl(4)	2.740(1)
Gd(1)−Cl(4)	3.003(1)	Gd(2)−Cl(3)	2.901(1)	Gd(3)−Cl(4)	2.966(1)	Gd(4)−Cl(3)	3.015(1)
Gd(1)−C(11)	2.694(5)	Gd(2)−C(21)	2.604(7)	Gd(3)−C(31)	2.620(6)	Gd(4)−C(41)	2.669(6)
Gd(1)−C(12)	2.643(4)	Gd(2)−C(22)	2.725(6)	Gd(3)−C(32)	2.653(5)	Gd(4)−C(42)	2.678(6)
Gd(1)−C(13)	2.684(5)	Gd(2)−C(23)	2.808(6)	Gd(3)−C(33)	2.813(6)	Gd(4)−C(43)	2.695(6)
Gd(1)−C(18)	2.729(5)	Gd(2)−C(28)	2.678(7)	Gd(3)−C(38)	2.709(7)	Gd(4)−C(48)	2.688(6)
Gd(1)−C(19)	2.748(6)	Gd(2)−C(29)	2.786(7)	Gd(3)−C(39)	2.803(6)	Gd(4)−C(49)	2.746(8)
Si(1)−N(1)−Si(2)	127.5(3)	Gd(1)−N(4)−Gd(2)	111.7(2)	Gd(2)−Cl(1)−Gd(3)	145.01(5)	Gd(1)−Cl(2)−Gd(4)	93.43(4)
Si(3)−N(2)−Si(4)	126.1(3)	Gd(4)−N(3)−Gd(3)	112.4(2)				
Cluster **IIb**							
Y(1)−O(1)	2.324(4)	Y(2)−N(1)	2.299(5)	Y(3)−N(2)	2.308(5)	Y(4)−N(3)	2.295(4)
Y(1)−N(4)	2.336(4)	Y(2)−N(4)	2.359(5)	Y(3)−N(3)	2.390(5)	Y(4)−O(3)	2.341(4)
Y(1)−Cl(4)	2.700(2)	Y(2)−O(4)	2.403(5)	Y(3)−O(2)	2.429(5)	Y(4)−Cl(2)	2.710(2)
Y(1)−Cl(2)	2.700(2)	Y(2)−Cl(1)	2.766(2)	Y(3)−Cl(1)	2.764(2)	Y(4)−Cl(3)	2.725(2)
Y(1)−Cl(3)	3.016(2)	Y(2)−Cl(4)	2.944(2)	Y(3)−Cl(3)	2.885(2)	Y(4)−Cl(4)	3.001(2)
Y(1)−C(11)	2.638(5)	Y(2)−C(21)	2.603(5)	Y(3)−C(31)	2.592(6)	Y(4)−C(41)	2.651(4)
Y(1)−C(12)	2.650(5)	Y(2)−C(22)	2.655(5)	Y(3)−C(32)	2.680(6)	Y(4)−C(42)	2.612(3)
Y(1)−C(13)	2.688(6)	Y(2)−C(23)	2.796(5)	Y(3)−C(33)	2.794(5)	Y(4)−C(43)	2.663(4)
Y(1)−C(18)	2.650(5)	Y(2)−C(28)	2.716(5)	Y(3)−C(38)	2.643(5)	Y(4)−C(48)	2.690(5)
Y(1)−C(19)	2.755(5)	Y(2)−C(29)	2.811(5)	Y(3)−C(39)	2.755(5)	Y(4)−C(49)	2.681(4)
Si(1)−N(1)−Si(2)	125.6(3)	Y(4)−N(3)−Y(3)	112.6(2)	Y(3)−Cl(1)−Y(2)	146.29(6)	Y(1)−Cl(2)−Y(4)	94.36(5)
Si(3)−N(2)−Si(4)	127.8(3)	Y(1)−N(4)−Y(2)	112.1(2)				
Cluster **IIIa**							
Gd(1)−N(3)	2.433(3)	Gd(1)−C(11)	2.773(5)	Gd(2)−C(21)	2.589(7)	Gd(3)−C(31)	2.672(4)
Gd(1)−N(2)	2.438(4)	Gd(1)−C(12)	2.756(6)	Gd(2)−C(22)	2.693(5)	Gd(3)−C(32)	2.652(6)
Gd(1)−N(1)	2.511(4)	Gd(1)−C(13)	2.780(6)	Gd(2)−C(23)	2.848(6)	Gd(3)−C(33)	2.767(6)
Gd(2)−N(3)	2.371(3)	Gd(1)−C(18)	2.733(5)	Gd(2)−C(28)	2.665(7)	Gd(3)−C(38)	2.796(4)
Gd(2)−N(4)	2.217(5)	Gd(1)−C(19)	2.780(5)	Gd(2)−C(29)	2.802(6)	Gd(3)−C(39)	2.869(6)
Gd(3)−N(1)	2.315(4)	Gd(1)−Cl(1)	2.804(2)	Gd(2)−Cl(2)	2.785(1)	Gd(3)−O(2)	2.431(3)
Gd(3)−N(2)	2.427(3)	Gd(1)−Cl(2)	2.734(2)	Gd(2)−O(3)	2.390(3)	Gd(3)−O(1)	2.490(3)
						Gd(3)−Cl(1)	2.793(2)
Gd(1)−N(1)-Gd(3)	93.2(1)	Gd(1)−N(3)−Si(2)	95.4(2)	N(1)−Si(2)−N(3)	103.4(2)	Gd(1)−Cl(1)−Gd(3)	77.69(4)
Gd(1)−N(2)−Gd(3)	92.3(1)	Gd(2)−N(3)−Gd(1)	106.7(1)			Gd(2)−Cl(2)−Gd(1)	88.58(4)
Cluster **IIIb**							
Er(1)−N(1)	2.453(3)	Er(1)−C(11)	2.684(4)	Er(2)−C(21)	2.591(5)	Er(3)−C(31)	2.670(4)
Er(1)−N(2)	2.381(3)	Er(1)−C(12)	2.668(4)	Er(2)−C(22)	2.687(4)	Er(3)−C(32)	2.609(5)
Er(1)−N(3)	2.383(3)	Er(1)−C(13)	2.722(5)	Er(2)−C(23)	2.802(4)	Er(3)−C(33)	2.697(5)
Er(2)−N(3)	2.308(3)	Er(1)−C(18)	2.745(4)	Er(2)−C(28)	2.661(5)	Er(3)−C(38)	2.798(4)
Er(2)−N(4)	2.233(4)	Er(1)−C(19)	2.749(4)	Er(2)−C(29)	2.821(4)	Er(3)−C(39)	2.880(5)
Er(3)−N(1)	2.247(3)	Er(1)−Cl(2)	2.602(2)	Er(2)−Cl(2)	2.663(2)	Er(3)−Cl(1)	2.746(1)
Er(3)−N(2)	2.388(3)	Er(1)−Cl(1)	2.779(1)	Er(2)−O(3)	2.374(3)	Er(3)−O(1)	2.407(3)
						Er(3)−O(2)	2.419(3)
Er(3)−N(1)−Er(1)	93.7(1)	Er(1)−N(3)−Er(2)	104.4(1)	N(1)−Si(2)−N(3)	102.4(2)	Er(1)−Cl(1)−Er(3)	76.75(3)
Er(1)−N(2)−Er(3)	92.0(1)	Si(2)−N(3)−Er(1)	95.7(1)			Er(1)−Cl(2)−Er(2)	89.52(5)

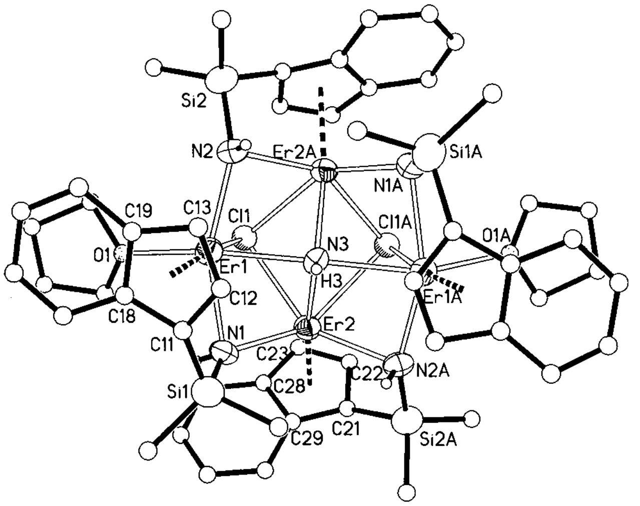
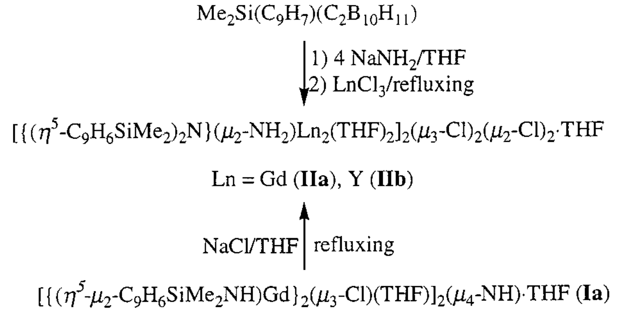


Figure 1. Molecular structure of $[\{(\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Er\}_2(\mu_3\text{-}Cl)(THF)]_2(\mu_4\text{-}NH)\cdot THF$ (**Ia**) (the solvated THF molecule is not shown).

Scheme 2



comparable to those of Ln−Cl (μ_3-Cl) distances found in the lanthanide analogues.[19]

Synthesis and Characterization of $[\{(\eta^5\text{-}C_9H_6SiMe_2)_2N\}(\mu_2\text{-}NH_2)Ln_2(THF)_2]_2(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\cdot OC_4H_8$. Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with 4 equiv of $NaNH_2$ at room temperature for 20 h, followed by reaction with 1 equiv of $LnCl_3$ in THF at reflux temperature overnight, after workup, gave another type of tetranuclear organolanthanide cluster, $[\{(\eta^5\text{-}C_9H_6SiMe_2)_2N\}(\mu_2\text{-}NH_2)Ln_2(THF)_2]_2(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\cdot OC_4H_8$ (Ln = Gd (**IIa**), Y (**IIb**)), in moderate yield. Cluster **IIa** can also be preapred in 38% isolated yield by refluxing a mixture of $[\{\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Gd\}_2(\mu_3\text{-}Cl)(THF)]_2(\mu_4\text{-}NH)\cdot OC_4H_8$ (**Ia**) and excess NaCl in THF. The above transformations are outlined in Scheme 2. As for cluster type **I**, these two clusters are air- and moisture-sensitive and they are soluble in THF, DME, and pyridine and slightly soluble in toluene but insoluble in *n*-hexane.

The two clusters have almost identical IR spectra, showing a characteristic N−H absorption at about 3260 cm^{-1}. The ^1H NMR spectrum of **IIb** exhibits two sets of indenyl resonances, four sets of methyl resonances, and a broad peak at 4.68 ppm attributable to the NH_2^- protons, which is consistent with its ^{13}C NMR spectrum. In contrast, the ^1H NMR spectrum of **IIa** is not informative, giving several very broad, unresolved resonances.

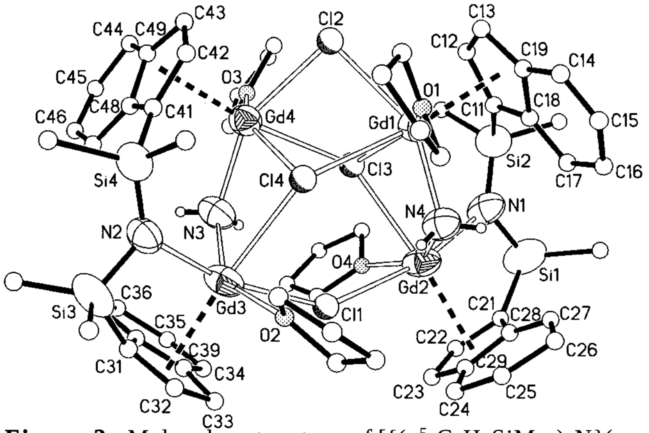


Figure 2. Molecular structure of $[\{(\eta^5\text{-}C_9H_6SiMe_2)_2N\}(\mu_2\text{-}NH_2)Gd_2(THF)_2]_2(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\cdot THF$ (**IIa**) (the solvated THF molecule is not shown).

The solid-state structures of **IIa** and **IIb** derived from single-crystal X-ray analyses reveal that they are another type of tetranuclear cluster, are isostructural and isomorphous, and also show one THF of solvation for each structure. As shown in Figure 2, the structure consists of a distorted-tetrahedral arrangement of four metals from two $[\{(\eta^5\text{-}C_9H_6SiMe_2)_2N\}(\mu_2\text{-}NH_2)Ln_2(THF)_2]^{2+}$ units that are connected by two doubly bridging μ_2-Cl atoms spanning Ln(1), Ln(4) and Ln(2), Ln(3) and two triply bridging μ_3-Cl atoms spanning Ln(1), Ln(2), Ln(4) and Ln(1), Ln(3), Ln(4), respectively. Each metal is either η^5-bound to one indenyl group and σ-bound to one oxygen atom, one nitrogen atom, and three chloride atoms (for Ln(1) and Ln(4)) or η^5-bound to one indenyl group and σ-bound to one oxygen atom, two nitrogen atoms, and two chloride atoms (for Ln(2) and Ln(3)) in a distorted-octahedral geometry with a formal coordination number of 8.

The average Ln−N($[\{(C_9H_6)SiMe_2\}_2N]^{3-}$) distances of 2.343(4) Å in **IIa** and 2.304(5) Å in **IIb** are shorter than the average Ln−N(NH_2^-) distances of 2.376(4) Å in **IIa** and 2.345(5) Å in **IIb**, respectively, due to the different coordination numbers of nitrogen atoms. These measured values can be compared to the 2.426(7) Å Gd−N(μ_2-NHSiMe$_2$(indenyl)) distance in **Ia**, the 2.395(4) Å Er−N(μ_2-NHSiMe$_2$(indenyl)) distance in **Ib**, the 2.256(7) and 2.396(7) Å Y−N distances in $Y[N(SiMe_2CHPMe_2)(SiMe_2CH_2PMe_2)][N(SiMe_2CH_2PMe_2)_2]$,[20] the 2.315(3) and 2.236(3) Å Y−N distances in (aminotroponiminato)yttrium amide,[21] the 2.315(5) Å Y−N distance in a tridentate linked amidocyclopentadienyl yttrium complex,[22] the 2.313(3)−2.330(3) Å distances in $[\{P_2N_2\}Y]_2[\eta^6{:}\eta^6\text{-}(C_6H_5)_2]$ ($P_2N_2 = [PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]$),[23] the 2.237(4) Å distance in $[Me_2Si(C_9H_5\text{-}2\text{-}Me)_2]Y[N(SiHMe_2)_2]$,[24] the 2.442(5)−2.620(6) Å distances in $[Li(Py)(TMSPyAm)_4Y]$ (TMSPyAm = (trimethyl-

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silyl)(4-methylpyridinyl-2)amido),[25] and the 2.54(2) Å distance in $[Y_2(\mu\text{-NHC}_6H_3Me_2\text{-}2,6)_2(\mu\text{-Cl})(NHC_6H_3Me_2\text{-}2,6)_4(THF)_2]^-$.[26] The average Gd−C distance of 2.709(6) Å is shorter than that of 2.751(14) Å in **Ia**. The average Y−C distance of 2.686(6) Å in **IIb** is close to that of 2.70(4) Å in $[(C_9H_7)Y(\mu\text{-OCMe}_3)(OCMe_3)]_2$[27] and 2.682(6) Å in $(CH_3OCH_2CH_2C_9H_6)_2YCl$.[18b] The average Ln−Cl(μ_3-Cl) distances of 2.898(1) Å in **IIa** and 2.878(2) Å in **IIb** are longer than the average Ln−Cl(μ_2-Cl) distances of 2.774(2) in **IIa** and 2.735(2) Å in **IIb** but are comparable with the average Gd−Cl(μ_3-Cl) distance of 2.852(2) Å in **Ia**.

Synthesis and Characterization of $[(\eta^5\text{-C}_9H_6SiMe_2)_2N][\mu_2,\mu_2\text{-Me}_2Si(NH)_2](\eta^5\text{-}\mu_2\text{-C}_9H_6SiMe_2NH)(\mu_2\text{-Cl})_2Ln_3(THF)_3$. Reaction of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with 8 equiv of $NaNH_2$ in THF at room temperature for 20 h, followed by treatment with 1 equiv of $LnCl_3$ at room temperature, after workup, produced the novel trinuclear organolanthanide clusters $[(\eta^5\text{-C}_9H_6SiMe_2)_2N][\mu_2,\mu_2\text{-Me}_2Si(NH)_2](\eta^5\text{-}\mu_2\text{-C}_9H_6SiMe_2NH)(\mu_2\text{-Cl})_2Ln_3(THF)_3$ in moderate yield (Scheme 3). These clusters are air- and moisture-sensitive; they are soluble in THF and pyridine and slightly soluble in toluene but insoluble in *n*-hexane.

Scheme 3

$$Me_2Si(C_9H_7)(C_2B_{10}H_{11}) \xrightarrow[\text{(2) LnCl}_3\text{/room temp}]{\text{(1) 8NaNH}_2\text{/THF}} [(\eta^5\text{-C}_9H_6SiMe_2)_2N][\mu_2,\mu_2\text{-Me}_2Si(NH)_2]\text{-}(\eta^5\text{-}\mu_2\text{-C}_9H_6SiMe_2NH)(\mu_2\text{-Cl})_2Ln_3(THF)_3$$

Ln = Gd (**IIIa**), Er (**IIIb**)

The IR spectra of these two clusters are quite similar, showing a characteristic N−H absorption at about 3270 cm^{-1}. Similar to those of clusters **Ia**−**c**, the ^{1}H NMR spectra of **IIIa**,**b** are not very informative. Thus, the formulation of the clusters is based primarily on their single-crystal X-ray analyses and elemental analyses.

X-ray diffraction studies reveal that both **IIIa** and **IIIb** are trinuclear clusters and they are isostructural and isomorphous. Their representative structure is shown in Figure 3. The five atoms Er(1), Er(2), Er(3), N(1), and N(4) are almost coplanar, defining a pentagonal plane. The doubly bridging Cl(1) and N(3) atoms are located below this plane, while the other two doubly bridging atoms of Cl(2) and N(2) sit above the plane. It is noteworthy that this type of cluster contains two kinds of indenyl ligands, $[(C_9H_6)SiMe_2NH]^{2-}$ and $[\{(C_9H_6)SiMe_2\}_2N]^{3-}$, observed in the above-mentioned type **I** and **II** clusters, respectively. Each metal has a unique coordination environment; two of them adopt a distorted-octahedral geometry with a formal coordination number of 8, and the other adopts a distorted-trigonal-bipyramidal geometry with a formal coordination number of 7.

The average Ln−N(2)(μ_2-NHSiMe$_2$(C$_9$H$_6$)) distances of 2.432(4) Å in **IIIa** and 2.384(4) Å in **IIIb** are close to the corresponding values of 2.426(7) Å in **Ia** and 2.395(4) Å in **Ib**, respectively. The Ln−N(4)([(C$_9$H$_6$)SiMe$_2$]$_2$N) distances of 2.217(5) Å in **IIIa** and 2.233(4) Å in **IIIb** are shorter than the corresponding values of 2.343(4) Å in **IIa** and 2.305(6) Å in **IIb**. The average Ln−N(1) distances are shorter than the average Ln−N(3) distances. These differences should be due to the different coordination number of the metals;[14] for instance, the 2.206(2) Å Er−N distance in Er[N(*t*-Bu)(SiMe$_2$H)]$_3$ is even shorter than that in **IIIb**.[28] It is, however, not clear why the Gd(2)−N(4) distance is shorter than the corresponding Er(2)−N(4) distance. The average Ln−Cl(μ_2-Cl) distances are comparable to those observed in **IIa**,**b**, and the average Ln−C distances are comparable to those found in **Ia**−**c** and **IIa**,**b**.

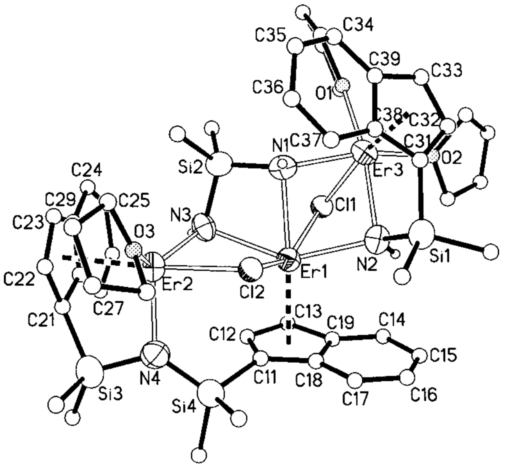

Figure 3. Molecular structure of $[(\eta^5\text{-C}_9H_6SiMe_2)_2N][\mu_2,\mu_2\text{-Me}_2Si(NH)_2](\eta^5\text{-}\mu_2\text{-C}_9H_6SiMe_2NH)(\mu_2\text{-Cl})_2Er_3(THF)_3$ (**IIIb**).

Discussion

Three novel types of organolanthanide clusters mentioned above are the first examples of organolanthanide indenyl clusters to be reported. Clusters **Ia**−**c** also represent the first organometallic clusters containing a central μ_4-NH group. These clusters were prepared in moderate yield, and all experiments are reproducible. The formation of these clusters are very interesting. On the basis of the ^{11}B NMR results, the Si−C(cage) bond is broken after mixing $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with excess $NaNH_2$ in THF. The *o*-carborane can be recovered by sublimation in over 70% yield under vacuum. It has been documented that $NaNH_2$ can serve as both base[29] and nucleophile.[30] It is reasonable to suggest that excess $NaNH_2$ deprotonates the acidic proton of the indenyl group and then attacks the Si atom to afford the intermediate $(C_9H_6)SiMe_2NH_2^-$; it reacts further with excess $NaNH_2$ to generate the new ligands $C_9H_6SiMe_2NH^{2-}$, $(C_9H_6SiMe_2)_2N^{3-}$, $Me_2Si(NH)_2^{2-}$, and NH^{2-} as shown in Scheme 4. Self-assembly of $LnCl_3$ and new

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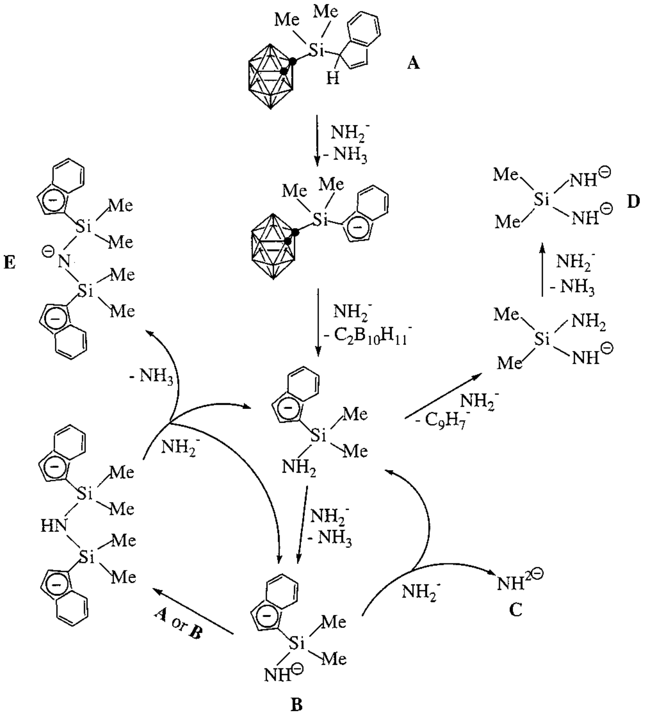
[30] $NaNH_2$ was suggested to be an intermediate in the reaction of $MeSiCl_3$ with Na in liquid NH_3 leading to the formation of $(MeSi)_6(NH)_9$; see: Räke, B.; Roesky, H. W.; Usón, I.; Müller, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1432.

Scheme 4



ligands derived from the reactions between $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ and excess $NaNH_2$ in THF gives tetranuclear clusters of types **I** and **II** and trinuclear clusters of type **III**, respectively. Cluster type **I** can be converted into type **II** in the presence of Cl^- in THF at reflux temperature, as indicated in Scheme 2. This transformation may occur in a way similar to that for the formation of $[(n\text{-Bu})N\{SiMe_2(C_9H_6)\}_2]ZrCl_2$ from $[(n\text{-Bu})NHSiMe_2(C_9H_6)]_2ZrCl_2$ or $[(n\text{-Bu})N\{SiMe_2(C_5H_4)\}_2]ZrCl_2$ from $[(n\text{-Bu})NHSiMe_2(C_5H_4)]_2ZrCl_2$.[31] Attempts to prepare the intermediate $(C_9H_7)SiMe_2NH_2$ from the reaction of $(C_9H_7)SiMe_2Cl$[8] with liquid NH_3 failed.[32] Direct interaction between $(C_9H_7)SiMe_2Cl$, excess $NaNH_2$, and $LnCl_3$ is very complicated; no pure compound was isolated.

Conclusion

Three types of novel organolanthanide clusters, $[\{(\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Ln\}_2(\mu_3\text{-}Cl)(THF)]_2(\mu_4\text{-}NH)\cdot n$THF (**I**), $[\{(\eta^5\text{-}C_9H_6SiMe_2)_2N\}(\mu_2\text{-}NH_2)Ln_2(THF)_2]_2(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\cdot$THF (**II**), and $[(\eta^5\text{-}C_9H_6SiMe_2)_2N][\mu_2,\mu_2\text{-}Me_2Si(NH)_2](\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)(\mu_2\text{-}Cl)_2Ln_3(THF)_3$ (**III**), were prepared from unprecedented reactions between $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$, excess $NaNH_2$, and $LnCl_3$ in THF. They represent not only the first examples of organometallic clusters containing a central $\mu_4\text{-}NH^{2-}$ group but also the first organolanthanide indenyl clusters to be reported. In these reactions, $NaNH_2$ serves as both base and nucleophile so that the anionic species (new ligands) generated in the reaction systems will be dependent upon the amount of $NaNH_2$ used and reaction temperature.

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Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures giving atom-numbering schemes for clusters **Ia**−**c**, **IIa**,**b**, and **IIIa**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990572W

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