# Synthesis and properties of guanidinate derivatives of rare-earth metals. Molecular structures of the $\{(Me_3Si)_2NC(NPr^i)_2\}_2Y(\mu\text{-}Cl)_2Li(THF)_2$, $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ and $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(\mu^3\text{-}BH_4)_2(DME)$ complexes

*A. A. Trifonov,* G. G. Skvortsov, D. M. Lyubov, G. K. Fukin, E. A. Fedorova, and M. N. Bochkarev*

*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation. Fax: +7 (083 12) 66 1497. E-mail: trif@imoc.sinn.ru*

The reaction of anhydrous $SmCl_3$ with two equivalents of lithium *N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate in THF afforded the $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ complex (**1**) in 82% yield. Analogous reactions with $YCl_3$ and $GdCl_3$ produced the *ate*-complexes $\{(Me_3Si)_2NC(NPr^i)_2\}_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Y (**2**) and Gd (**3**)). The structures of complexes **1** and **2** were established by X-ray diffraction. The reaction of complex **1** with $NaBH_4$ in hexane (20 °C) followed by treatment with dimethoxyethane yielded the unexpected product, $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(\mu^3\text{-}BH_4)_2(DME)$ (**5**). X-ray diffraction study showed that both borohydride ligands in complex **5** are tridentate.

**Key words:** rare-earth metals, complexes, guanidinate ligand, *N*,*N* ligand, borohydride ligand, synthesis, structure.

Mono- and biscyclopentadienyl derivatives of rare-earth metals exhibit various and unusual chemical properties, which fact provided impetus for the extensive development of this area of chemistry in the last two decades.[1—5] In particular, rare-earth metal compounds have attracted considerable interest because alkyl, hydride, and borohydride complexes appeared to be active catalysts (or their precursors) for transformations of unsaturated substrates.[6—10] Taking into account that the chemical properties of rare-earth alkyl and hydride complexes depend substantially on the nature of stabilizing ligands,[11—13] it is of interest to study stoichiometric and catalytic reactions of related compounds in the non-cyclopentadienyl ligand coordination environment. Unlike sandwich- and half-sandwich-type alkyl and hydride derivatives, their analogs in the non-cyclopentadienyl coordination environment remain poorly known. Many research groups are interested in designing "hard" mono- and dianionic polydentate N- and/or O-coordinating ligands, which can sterically saturate the coordination sphere of the rare-earth atom, thus providing kinetic stability of complexes without a decrease in their reactivity.[14—16] We focused out attention on monoanionic tetrasubstituted guanidinate ligands whose electronic and steric properties can easily be modified[17] by replacing hydrocarbon groups at the nitrogen atoms. Recently, these ligands have been successfully used in the synthesis of new rare-earth complexes.[18—21] In the present study, we synthesized bis(guanidinate) chloride and monoguanidinate bis(tetraborohydride) derivatives of rare-earth metals and established the structures of the $\{(Me_3Si)_2NC(NPr^i)_2\}_2Y(\mu\text{-}Cl)_2Li(THF)_2$, $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$, and $\{(Me_3Si)_2NC(NPr^i)_2\}_2Sm(\mu^3\text{-}BH_4)_2(DME)$ complexes by X-ray diffraction.

## Results and Discussion

The reaction of anhydrous $SmCl_3$ with two equivalents of $\{(Me_3Si)_2NC(NPr^i)_2\}Li$, which was generated *in situ* from $[(Me_3Si)_2NLi(Et_2O)]$ and *N*,*N*′-diisopropylcarbodiimide, in THF (20 °C) produced the bis(guanidinate) chloride complex $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ (**1**). Complex **1** was isolated as bright-yellow crystals in 82% yield by extraction with toluene followed by recrystallization from hexane (Scheme 1).

The reactions of $YCl_3$ and $GdCl_3$ with two equivalents of lithium *N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate in THF followed by the above-described isolation afforded the mononuclear *ate*-complexes $\{(Me_3Si)_2NC(NPr^i)_2\}_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Y (**2**) and Gd (**3**)) (Scheme 2) as colorless crystals in 92 and 83% yields, respectively. The formation of complex **2** has been documented earlier;[19] however, this compound was not characterized.

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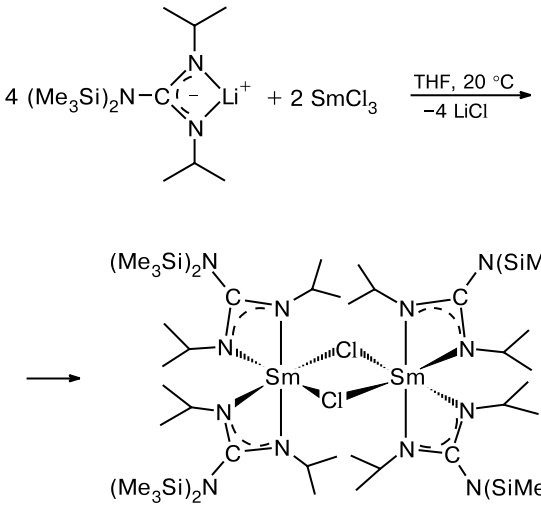
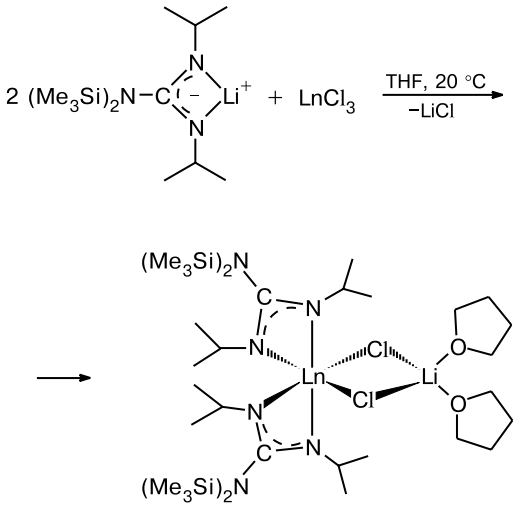
**Scheme 1**



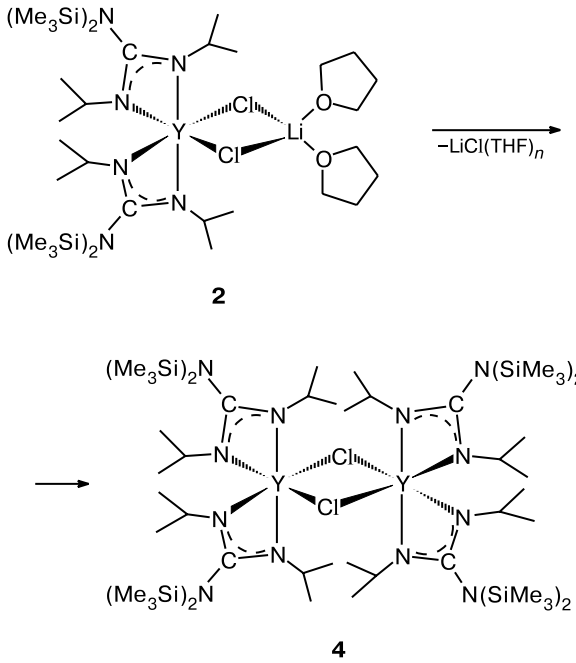

**Scheme 2**




Ln = Y (**2**), Gd (**3**)

The compositions and structures of rare-earth bis(guanidinate) chloride complexes prepared by the metathesis reactions of the corresponding trichlorides with lithium guanidinate depend both on the metal ion size and the conditions of the synthesis and isolation of the reaction product. Earlier, it has been demonstrated that this reaction, in the case of neodymium, affords the neutral dinuclear complex $[\{(Me_3Si)_2NC(NPr^i)_2\}_2NdCl]_2$,[22] whereas the ionic *ate*-complexes $\{(Me_3Si)_2NC(NPr^i)_2\}_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Yb[20] or Lu[21]) were prepared under analogous conditions for ytterbium and lutetium. In the case of yttrium, the composition of the resulting complex depends on the reaction conditions. The reaction in diethyl ether yielded the $[\{(Me_3Si)_2NC(NPr^i)_2\}_2YCl]_2$ dimer (**4**).[19] The reaction in THF, which is a stronger complex-forming agent, afforded (after analogous isolation) the *ate*-complex $\{(Me_3Si)_2NC(NPr^i)_2\}_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (**2**). Prolonged heating of complex **2** in hexane is accompanied by elimination of $LiCl(THF)_n$ and the formation of dimer **4** (Scheme 3).

**Scheme 3**




Therefore, it can be concluded that early lanthanides (Nd and Sm) are prone to form dinuclear bis(guanidinate) chlorides, whereas middle and late lanthanides (Gd, Yb, and Lu) are more prone to form *ate*-complexes. Yttrium can give both dinuclear and *ate*-complexes depending on the conditions of the synthesis and isolation of the product.

Compounds **1**—**3** are sensitive to atmospheric oxygen and moisture. Nevertheless, these compounds are stable during prolonged storage *in vacuo* or in an inert atmosphere at room temperature. Complexes **1**—**3** are readily soluble in ethereal solvents and aromatic and aliphatic hydrocarbons.

The $^1H$ NMR spectrum of diamagnetic complex **2** (benzene-$d_6$, 20 °C) shows the following set of signals belonging to the guanidinate ligands: a singlet at $\delta_H$ 0.48 assigned to the Me protons of the $N(SiMe_3)_2$ fragments and a doublet at $\delta_H$ 1.60 with the coupling constant $^3J_{H,H}$ = 6.2 Hz belonging to the Me protons of the isopropyl groups. The methine protons of the isopropyl groups give a well-resolved septet at $\delta_H$ 4.01 with $^3J_{H,H}$ = 6.4 Hz. In

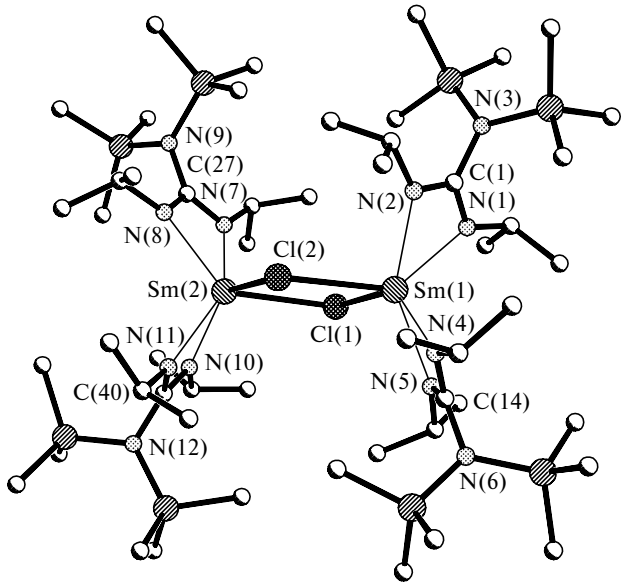



**Fig. 1.** Structure of the $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ complex (**1**).

the $^{13}C$ NMR spectrum, the guanidinate fragments are also characterized by one set of signals, which indicates that the two ligands are equivalent. The fact that the methylene protons of the THF molecules give broadened singlets in the $^1H$ NMR spectrum is evidence for lability of their coordination.

Transparent bright-yellow crystals of complex **1** suitable for X-ray diffraction study were grown by slow evaporation of a hexane solution at room temperature. Complex **1** crystallizes in the space group *Pc* with two molecules in the unit cell. The molecular structure of complex **1** is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. X-ray diffraction study showed that complex **1** exists in the crystalline state as dimers due to $\mu^2$-bridging coordination of two chloride ligands and it is isostructural with the neodymium analog, whose structure has been established earlier.[22] The coordination environment of the samarium atoms in **1** is formed by four nitrogen atoms of two bidentate guanidinate ligands and two chlorine atoms, resulting in the coordination number of six.

The Sm—Cl bonds in the planar four-membered $Sm_2Cl_2$ fragment are very similar in length (2.787(2)—2.796(2) Å) and are slightly longer than the corresponding bonds in the dinuclear metallocene analog $[(\eta^5\text{-}Bu^tC_5H_4)_2Sm(\mu\text{-}Cl)]_2$ (2.764(2)—2.767(2) Å).[23] Apparently, this fact is attributed to higher steric hindrance of the coordination environment of the metal atom and, correspondingly, to larger repulsion between the $L_2M$ fragments in the bis(guanidinate) derivative. The Cl—Sm—Cl bond angles in molecule **1** (76.02(5)° and 76.06(5)°) are slightly smaller than the corresponding angles in the $[(\eta^5\text{-}Bu^tC_5H_4)_2Sm(\mu\text{-}Cl)]_2$ complex (79.0(1)° and 78.6(1)°).[23] The chelate guanidinate ligands are bound to the central atom by two Sm—N bonds, one bond being substantially shorter than another bond (2.375(5)—2.396(6) and 2.435(5)—2.444(5) Å, respectively). The average Sm—N bond length in molecule **1** is 2.411 Å, which is substantially larger than the lengths of the $Sm^{III}$—N covalent bonds in the trivalent samarium derivatives $[(Me_3Si)_2NSmCl_2(THF)]_2$ (2.258—2.285 Å)[24] and $(C_5Me_5)_2SmN(SiMe_3)_2$ (2.301 Å)[25] and is similar to the bond lengths observed in the trivalent samarium complex with azobenzene $(C_5Me_5)_2SmN_2Ph_2(THF)$ (2.390—2.450 Å).[26] The nitrogen—carbon bonds in the NCN fragments coordinated to the metal atom are very similar in length, which is indicative of delocalization of the negative charge. In molecule **1**, the C(27)—Sm(2)—C(40) and C(1)—Sm(1)—C(14) bond angles (122.5(8)° and 124.49(17)°, respectively), which can be considered as analogs of the $Cp_{center}$—M—$Cp_{center}$ angles in metallocene complexes, are slightly smaller than those in the sandwich complex $[(\eta^5\text{-}Bu^tC_5H_4)_2Sm(\mu\text{-}Cl)]_2$ (127.5 and 126.3°).[23]

Transparent colorless crystals of complex **2** were grown by slow evaporation of its saturated solution in hexane at room temperature. Complex **2** crystallizes in the space group $P\bar{1}$ with two molecules in the unit cell (Fig. 2,

**Table 1.** Selected bond lengths (*d*) and bond angles (ω) in complex **1**

| Bond | *d*/Å | Bond | *d*/Å | Angle | ω/deg |
|---|---|---|---|---|---|
| Sm(1)—N(1) | 2.375(5) | Sm(2)—Cl(2) | 2.7956(17) | N(1)—Sm(1)—N(2) | 55.05(19) |
| Sm(1)—N(4) | 2.380(5) | N(1)—C(1) | 1.312(9) | N(4)—Sm(1)—N(5) | 55.67(17) |
| Sm(1)—N(5) | 2.444(5) | N(2)—C(1) | 1.319(9) | N(10)—Sm(2)—N(11) | 55.15(18) |
| Sm(1)—N(2) | 2.442(5) | N(3)—C(1) | 1.471(8) | N(8)—Sm(2)—N(7) | 55.30(18) |
| Sm(1)—Cl(1) | 2.7893(17) | N(4)—C(14) | 1.341(8) | Cl(1)—Sm(1)—Cl(2) | 76.06(5) |
| Sm(1)—Cl(2) | 2.7908(18) | N(5)—C(14) | 1.340(8) | Cl(1)—Sm(2)—Cl(2) | 76.02(5) |
| Sm(2)—N(10) | 2.378(5) | N(10)—C(40) | 1.320(9) | Sm(2)—Cl(1)—Sm(1) | 104.06(6) |
| Sm(2)—N(8) | 2.396(6) | N(11)—C(40) | 1.342(8) | Sm(1)—Cl(2)—Sm(2) | 103.79(6) |
| Sm(2)—N(11) | 2.435(5) | N(8)—C(27) | 1.331(8) | C(27)—Sm(2)—C(40) | 122.50(18) |
| Sm(2)—N(7) | 2.443(5) | N(7)—C(27) | 1.324(9) | C(1)—Sm(1)—C(14) | 124.49(17) |
| Sm(2)—Cl(1) | 2.7871(18) | | | | |

**Table 2.** Selected bond lengths (*d*) and bond angles (ω) in molecule **2**

| Bond | *d*/Å | Bond | *d*/Å | Angle | ω/deg |
|---|---|---|---|---|---|
| Y(1)—N(5) | 2.319(2) | N(1)—C(1) | 1.329(3) | N(5)—Y(1)—N(4) | 56.60(7) |
| Y(1)—N(1) | 2.331(2) | N(2)—C(1) | 1.338(3) | N(1)—Y(1)—N(2) | 56.65(7) |
| Y(1)—N(4) | 2.378(2) | N(4)—C(14) | 1.326(3) | Cl(2)—Y(1)—Cl(1) | 82.32(2) |
| Y(1)—N(2) | 2.383(2) | N(5)—C(14) | 1.322(3) | Cl(2)—Li(1)—Cl(1) | 96.44(18) |
| Y(1)—Cl(2) | 2.6607(8) | Y(1)—Cl(2) | 2.6607(8) | O(1)—Li(1)—O(2) | 104.4(2) |
| Cl(1)—Li(1) | 2.391(5) | O(1)—Li(1) | 1.931(6) | C(14)—Y(1)—C(1) | 128.59(7) |
| Cl(2)—Li(1) | 2.323(5) | O(2)—Li(1) | 1.946(6) | | |

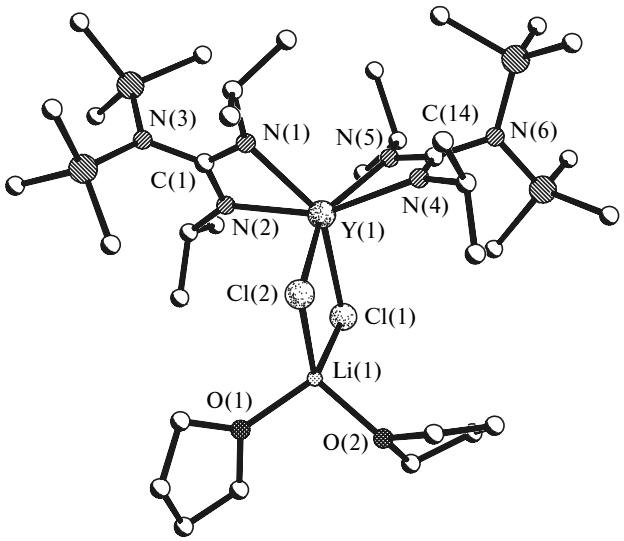



**Fig. 2.** Structure of the $\{(Me_3Si)_2NC(NPr^i)_2\}_2Y(\mu\text{-}Cl)_2Li(THF)_2$ complex (**2**).

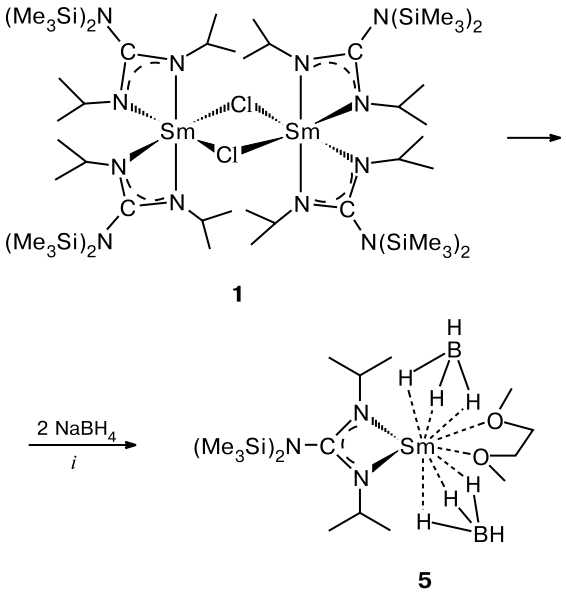
Table 2). X-ray diffraction study demonstrated that compound **2** is an *ate*-complex isostructural with the lutetium-containing analog prepared earlier.[21] The formal coordination number of the yttrium atom in molecule **2** is 6. The coordination polyhedron is formed by four nitrogen atoms of two bidentate guanidinate ligands and two bridging chlorine atoms, which link the yttrium and lithium atoms. The lithium atom is coordinated by two oxygen atoms of two THF molecules.

The yttrium—nitrogen bonds in complex **2** have rather similar lengths varying in the range of 2.319(2)—2.383(2) Å. However, one Y—N bond in each chelate ligand is slightly longer than another bond (Y(1)—N(5), 2.319(2) Å; Y(1)—N(4), 2.378(2) Å in one ligand; Y(1)—N(1), 2.331(2) Å; Y(1)—N(2), 2.383(2) Å in another ligand). The Y—N distances in molecule **2** are similar to the analogous bond lengths observed earlier in the related guanidinate and amidinate derivatives of yttrium $\{[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}Cl)\}_2$ (2.326(4)—2.388(4) Å),[19] $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$ (2.327(3)—2.389(3) Å),[27] and $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}Cl)_2Li(TMEDA)$ (2.334(2)—2.373(2) Å).[28] The carbon—nitrogen bond lengths in the four-membered metallacycles differ only slightly from each other (1.322(3)—1.338(3) Å), which is indicative of delocalization of the negative charge over the NCN fragments of the guanidinate ligands. The substantially longer N—C bond between the central carbon atom and the nitrogen atom of the $N(SiMe_3)_2$ group (1.434(4) and 1.4545(4) Å) is evidence that this bond is not involved in conjugation. The mutual arrangement of the $N(SiMe_3)_2$ groups and the isopropyl substituents of the guanidinate ligands relative to the NCN plane indicates that their mutual steric repulsion is minimum. The endocyclic N—Y—N bond angles in these metallacycles are 56.60(7)° and 56.65(7)°. The Y—Cl bonds (2.6607(8) and 2.6813(7) Å) in molecule **2** are slightly longer than the analogous bonds in the metallocene *ate*-complexes $Cp^*_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (2.646(2) and 2.655(2) Å)[29] and $[(1,3\text{-}Me_3Si)_2C_5H_3]_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (2.626(1) and 2.631(1) Å)[30] but are shorter that those in the related dinuclear complex $[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}Cl)\}_2$ (2.713(1) and 2.717(1) Å).[19] The C(1)—Y—C(14) bond angle in compound **2** is 128.59(7)°, which is slightly larger than the analogous bond angles in complexes **1** and $\{[(Me_3Si)_2NC(NPr^i)_2]_2Y(\mu\text{-}Cl)\}_2$ (123.1(1)°).[19] Apparently, this fact reflects the lower degree of steric hindrance of the coordination environment about the metal atom in the *ate*-complex compared to that in the dimer.

In recent years, borohydride derivatives of rare-earth metals have attracted growing interest[4,31—33] due to publications on their catalytic activity in controlled polymerization of both polar (methyl methacrylate[34] and ε-caprolactone[35]) and nonpolar (isoprene[36]) monomers. However, metallocene derivatives still prevail among these compounds.[4] The synthesis of the first borohydride derivative of lanthanide containing no Cp ligands, $[(2\text{-}C_5H_4N)CH_2N(CH_2CH_2NSiMe_3)_2Sm(\mu\text{-}Cl)]_2$, has been published recently.[34] We attempted to synthesize the samarium bis(guanidinate) borohydride complex by the reaction of complex **1** with $NaBH_4$ in hexane at room temperature for 14 h. After separation of NaCl that precipitated, treatment with dimethoxyethane, and recrystallization of the product from a toluene—hexane mixture, we unexpectedly isolated the monoguanidinate

bis(borohydride) complex $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(\mu^3\text{-}BH_4)_2(DME)$ (**5**) in 31% yield (Scheme 4).

**Scheme 4**




*i*. Hexane, 20 °C.

Evidently, the guanidinate ligands are redistributed either during the reaction or in the course of isolation giving rise to complex **5**. It should be noted that the only rare-earth bis(borohydride) complex $(\eta^5\text{-}C_5Pr^i_4H)Nd(\mu^3\text{-}BH_4)_2(THF)$ has been structurally characterized.[36]

Compound **5** was prepared as pale-yellow crystals sensitive to atmospheric oxygen and moisture. Complex **5** is readily soluble in THF and DME, moderately soluble in toluene, and poorly soluble in hexane. Transparent crystals of compound **5** suitable for X-ray diffraction study were grown by slow condensation of hexane into a concentrated solution of complex **5** in toluene at room temperature. Compound **5** crystallizes in the space group $P\bar{1}$

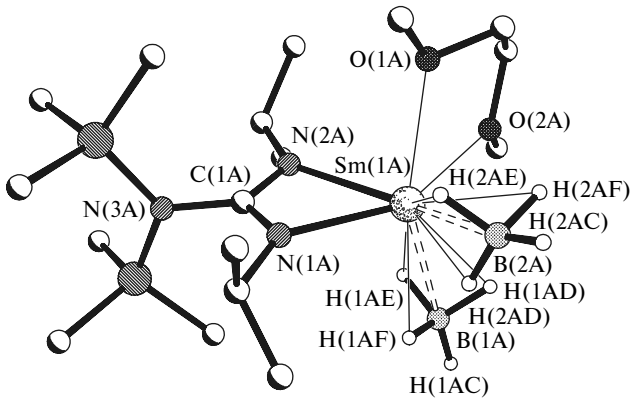



**Fig. 3.** Structure of the $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(\mu^3\text{-}BH_4)_2(DME)$ complex (**5**). One of two crystallographically independent molecules is shown.

(two crystallographically independent molecules) with four molecules per unit cell (Fig. 3, Table 3). X-ray diffraction study demonstrated that complex **5** is mononuclear. The samarium atom in compound **5** is coordinated by two nitrogen atoms of the chelate guanidinate ligand, two oxygen atoms of the DME molecule, and two $BH_4$ groups. The borohydride fragments in molecule **5**, like that in the dimeric sandwich samarium complex $[(1,3\text{-}Bu^t_2\text{-}C_5H_3)_2Sm(BH_4)]_2$,[37] are $\mu^3$-coordinated to the metal atom through three hydrogen atoms. The Sm—B distances in molecule **5** (2.607(3), 2.615(4), 2.614(3), and 2.616(3) Å) are substantially shorter than those in the dinuclear complex $[(1,3\text{-}Bu^t_2\text{-}C_5H_3)_2Sm(BH_4)]_2$ (2.833(6) and 2882(6) Å).[37]

The tridentate coordination of the borohydride ligands is confirmed also by the IR spectrum of compound **5**, which shows four broad bands at 2164, 2223, 2337, and 2451 $cm^{-1}$ corresponding to these ligands.[4] The Sm—N distances in molecule **5** differ only slightly from each other (2.395(2), 2.374(2); 2.377(2), 2.388(2) Å) and are noticeably shorter than the corresponding bonds in complex **1**. The Sm—O bond lengths are 2.5059(19) and 2.5153(17) Å.

**Table 3.** Selected bond lengths (*d*) and bond angles (ω) in molecule **5** (for both crystallographically independent molecules **A** and **B**)

| Bond | *d*/Å | Bond | *d*/Å | Angle | ω/deg |
|---|---|---|---|---|---|
| **A** | | **B** | | **A** | |
| Sm(1A)—N(1A) | 2.374(2) | Sm(1B)—N(1B) | 2.377(2) | N(1A)—Sm(1A)—N(2A) | 55.84(7) |
| Sm(1A)—N(2A) | 2.395(2) | Sm(1B)—N(2B) | 2.388(2) | O(1A)—Sm(1A)—O(2A) | 63.64(6) |
| Sm(1A)—O(1A) | 2.5059(19) | Sm(1B)—O(1B) | 2.482(2) | B(2A)—Sm(1A)—B(1A) | 102.52(13) |
| Sm(1A)—O(2A) | 2.5153(17) | Sm(1B)—O(2B) | 2.5156(18) | **B** | |
| Sm(1A)—B(2A) | 2.607(3) | Sm(1B)—B(1B) | 2.614(3) | N(1B)—Sm(1B)—N(2B) | 55.98(7) |
| Sm(1A)—B(1A) | 2.615(4) | Sm(1B)—B(2B) | 2.616(3) | O(1B)—Sm(1B)—O(2B) | 64.17(6) |
| N(1A)—C(1A) | 1.321(3) | C(1B)—N(1B) | 1.328(3) | B(1B)—Sm(1B)—B(2B) | 102.49(12) |
| C(1A)—N(2A) | 1.337(3) | C(1B)—N(2B) | 1.336(3) | | |
| C(1A)—N(3A) | 1.431(3) | C(1B)—N(3B) | 1.433(3) | | |

To summarize, the results of our study demonstrated that the tetrasubstituted guanidinate ligands are alternative to the Cp anions and allow one to prepare stable rare-earth complexes, in which the central atom has a low coordination number. The exchange reactions of anhydrous rare-earth halides with lithium guanidinate in a molar ratio of 1 : 2 can produce both dinuclear and bis(guanidinate) chloride *ate*-complexes. Early lanthanides (Nd and Sm) are prone to form dinuclear bis(guanidinate) chlorides, whereas middle and late lanthanides (Gd, Yb, and Lu) are more prone to give *ate*-complexes. Yttrium can form both dinuclear and *ate*-complexes depending on the conditions of the synthesis and isolation of the reaction product.

## Experimental

Syntheses were carried out under conditions precluding exposure to atmospheric oxygen and moisture with the use of the standard Schlenk technique. The solvents THF, DME, hexane, and toluene were dried with sodium benzophenone ketyl, thoroughly degassed, and condensed into a reaction tube under vacuum immediately before use. The IR spectra were recorded on a Specord M80 instrument; samples were prepared as Nujol mulls. The $^1$H and $^{13}$C NMR spectra were measured on a Bruker DPX 200 instrument. The chemical shifts are given on the δ scale relative to the shifts of the residual protons of the deuterated solvents. Anhydrous $LnCl_3$ [38] and $(Me_3Si)_2NLi(Et_2O)$[39] were prepared according to known procedures. Commercial *N*,*N*′-diisopropylcarbodiimide (Acros) was used after drying with molecular sieves A4 and vacuum condensation.

**Samarium(III) bis[*N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate] chloride, $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ (1).** Samarium chloride $SmCl_3$ (0.514 g, 2.00 mmol) was added to a solution of lithium guanidinate, which was prepared by the reaction of $(Me_3Si)_2NLi(Et_2O)$ (0.964 g, 4.00 mmol) with *N*,*N*′-diisopropylcarbodiimide (0.505 g, 4.00 mmol) in THF (40 mL). The reaction mixture was stirred at 40 °C for 24 h. Tetrahydrofuran was removed by vacuum condensation and the solid residue was extracted with toluene to separate LiCl that formed. The toluene extract was filtered and the toluene was removed *in vacuo* at room temperature. After recrystallization of the residue from hexane, yellow crystals of complex **1** were obtained in a yield of 2.490 g (82%). Found (%): C, 40.77; H, 8.93; Sm, 19.97. $C_{52}H_{128}Cl_2N_{12}Si_8Sm_2$. Calculated (%): C, 41.14; H, 8.43; Sm, 19.81. IR (Nujol mulls), ν/cm$^{-1}$: 1630, 1310, 1250, 1200, 1040, 950, 830.

**Lithium bis[*N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate] dichloroyttrate(III) bis(tetrahydrofuranate), $\{(Me_3Si)_2NC(NPr^i)_2\}_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (2).** Yttrium chloride $YCl_3$ (0.512 g, 2.62 mmol) was added to a solution of lithium guanidinate, which was prepared by the reaction of $(Me_3Si)_2NLi(Et_2O)$ (1.262 g, 5.24 mmol) with *N*,*N*′-diisopropylcarbodiimide (0.660 g, 5.24 mmol) in THF (50 mL). The reaction mixture was stirred at 20 °C for 4 h. Tetrahydrofuran was removed by vacuum condensation and the solid residue was extracted with toluene to separate LiCl that formed. The toluene extract was filtered and the toluene was removed *in vacuo* at room temperature. After recrystallization of the residue from hexane, colorless crystals of complex **2** were obtained in a yield of 2.128 g (92%). Found (%): C, 46.00; H, 8.39; Y, 10.23. $C_{34}H_{79}Cl_2LiN_6O_2Si_4Y$. Calculated (%): C, 46.24; H, 8.94; Y, 10.06. IR (Nujol mulls), ν/cm$^{-1}$: 1639, 1323, 1254, 1203, 1052, 954, 840, 756, 684. $^1$H NMR (20 °C, benzene-$d_6$), δ: 0.48 (s, 36 H, $N(SiMe_3)_2$); 1.47 (br.s, 8 H, THF); 1.60 (d, 24 H, $CH(C\underline{H}_3)_2$, $^3J_{H,H}$ = 6.2 Hz); 3.76 (br.s, 8 H, THF); 4.01 (sept, 4 H, $C\underline{H}(CH_3)_2$, $^3J_{H,H}$ = 6.2 Hz). $^{13}$C NMR (20 °C, benzene-$d_6$), δ: 2.9 ($N(SiMe_3)_2$); 25.4 (β-$CH_2$, THF); 27.3 ($CH(CH_3)_2$); 46.2 ($\underline{C}H(CH_3)_2$); 68.8 (α-$CH_2$, THF); 168.9 ($CN_3$).

**Lithium bis[*N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate] dichlorogadolinate bis(tetrahydrofuranate), $\{(Me_3Si)_2NC(NPr^i)_2\}_2Gd(\mu\text{-}Cl)_2Li(THF)_2$ (3).** Gadolinium chloride $GdCl_3$ (0.870 g, 3.30 mmol) was added to a solution of lithium guanidinate, which was prepared by the reaction of $(Me_3Si)_2NLi(Et_2O)$ (1.590 g, 6.60 mmol) with *N*,*N*′-diisopropylcarbodiimide (0.831 g, 6.60 mmol) in THF (40 mL). The reaction mixture was stirred at 20 °C for 2 h. Tetrahydrofuran was removed by vacuum condensation and the solid residue was extracted with toluene to separate LiCl that formed. The toluene extract was filtered and the toluene was removed *in vacuo* at room temperature. After recrystallization of the residue from hexane, colorless crystals of complex **3** were obtained in a yield of 2.600 g (83%). Found (%): C, 45.33; H, 8.38; Gd, 16.82. $C_{34}H_{79}Cl_2LiN_6O_2Si_4Gd$. Calculated (%): C, 45.86; H, 8.16; Gd, 16.67. IR (Nujol mulls), ν/cm$^{-1}$: 1638, 1322, 1254, 1200, 1170, 1138, 1123, 1050, 954, 838, 757, 684.

**Samarium(III) [*N*,*N*′-diisopropyl-*N*″-bis(trimethylsilyl)guanidinate] bis(borohydride) dimethoxyethanate $\{(Me_3Si)_2NC(NPr^i)_2\}Sm(\mu^3\text{-}BH_4)_2(DME)$ (5).** Sodium borohydride (0.027 g, 0.71 mmol) was added to a solution of $[\{(Me_3Si)_2NC(NPr^i)_2\}_2SmCl]_2$ (1.030 g, 0.68 mmol) in hexane (50 mL). The reaction mixture was stirred at 20 °C for 14 h. The hexane solution was filtered and the precipitate was twice extracted with hexane (2×15 mL). The extracts were combined and the hexane was removed by vacuum condensation. The yellow solid residue was dissolved in DME (5 mL), and the solvent was evaporated *in vacuo* at room temperature. The yellow finely crystalline compound was dissolved in toluene (30 mL). Slow condensation of hexane into a toluene solution at room temperature afforded yellow crystals of complex **5** in a yield of 0.120 g (31%). Found (%): C, 36.07; H, 8.49; Sm, 27.17. $C_{17}H_{50}B_2N_3O_2Si_2Sm$. Calculated (%): C, 36.69; H, 8.98; Sm, 27.03. IR (Nujol mulls), ν/cm$^{-1}$: 2451, 2337, 2223, 2164, 1610, 1326, 1255, 1168, 1098, 1052, 955, 841, 759, 688.

**Transformation of $\{(Me_3Si)_2NC(NPr^i)_2\}_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (2) into $[\{(Me_3Si)_2NC(NPr^i)_2\}_2YCl]_2$ (4).** A solution of complex **2** (1.012 g, 1.14 mmol) in hexane (20 mL) was heated at 60 °C for 6 h, after which a colorless precipitate was obtained. The solution was filtered and concentrated *in vacuo* to prepare a viscous oil. Upon storage of the oil at 0 °C for 3 days, colorless crystals of complex **4** were obtained. The crystals were washed with cold pentane and dried *in vacuo* (0.5 h, 20 °C). Complex **4** was isolated in a yield of 0.718 g (90%). Found (%): C, 44.20; H, 8.76; Y, 12.99. $C_{52}H_{128}Cl_2N_{12}Si_8Y_2$. Calculated (%): C, 44.77; H, 9.25; Y, 12.76. IR (Nujol mulls), ν/cm$^{-1}$: 1644, 1330, 1262, 1211, 948, 751, 680. $^1$H NMR (20°C, benzene-$d_6$), δ: 0.41 (br.s, 72 H, $N(SiMe_3)_2$); 1.50 and 1.56 (both d, 24 H each, $CHC\underline{H}_3$, $^3J_{H,H}$ = 6.2 Hz); 4.00 (m, 8 H, $C\underline{H}CH_3$).

**Table 4.** Crystallographic parameters of complexes **1**, **2**, and **5**

| Parameter | **1** | **2** | **5** |
|---|---|---|---|
| Molecular formula | $C_{52}H_{128}Cl_2N_{12}Si_8Sm_2$ | $C_{34}H_{79}Cl_2LiN_6O_2Si_4Y$ | $C_{17}H_{50}B_2N_3O_2Si_2Sm$ |
| Molecular weight | 1517.9 | 883.1 | 556.7 |
| Space group | *Pc* | *P*1 | *P*1 |
| *a*/Å | 13.177(3) | 9.8479(7) | 8.3786(6) |
| *b*/Å | 14.744(3) | 14.8565(10) | 18.8839(13) |
| *c*/Å | 20.636(4) | 18.2910(12) | 19.0790(13) |
| α/deg | 90 | 75.887(2) | 74.0040(10) |
| β/deg | 96.688(5) | 86.428(2) | 79.3790(10) |
| γ/deg | 90 | 74.9290(10) | 86.5040(10) |
| *V*/Å$^3$ | 3981.9(15) | 2506.0(3) | 2851.9(3) |
| *Z* | 2 | 2 | 4 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.266 | 1.170 | 1.297 |
| μ/mm$^{-1}$ | 1.685 | 1.398 | 2.158 |
| Scan range, θ/ω | 1.38—24.99 | 2.06—22.50 | 1.12—25.00 |
| Number of measured reflections | 21617 | 10900 | 22391 |
| Number of reflections with $I > 2\sigma$ | 10881 ($R_{int}$ = 0.0619) | 6512 ($R_{int}$ = 0.0235) | 9970 ($R_{int}$ = 0.0181) |
| Number of parameters in refinement | 686 | 541 | 551 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0426 | 0.0459 | 0.0321 |
| $wR_2$ ($I > 2\sigma(I)$) | 0.0742 | 0.1192 | 0.0897 |

**X-ray diffraction study.** X-ray diffraction data sets were collected on an automated Smart APEX diffractometer (graphite monochromator, Mo-Kα radiation, φ—φ scanning technique, the exposure time was 10 s per frame) at 100 K for all complexes. Principal crystallographic characteristics are given in Table 4. All structures were solved by direct methods and refined by the least-squares method against $F^2_{hkl}$ with anisotropic displacement parameters for all nonhydrogen atoms. The H atoms in all complexes were placed in geometrically calculated positions and refined using a riding model, except for the H atoms in the $BH_4$ groups in the crystal structure of **5**, which were located from difference electron density maps and refined isotropically. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[40] Absorption corrections were applied using the SADABS program.[41]

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