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Mixed-ligand guanidinate derivatives of rare-earth metals. Molecular structures of $\{(Me_3Si)_2NC(N—\textit{cyclo}\text{-}Hex)_2\}Y[N(SiMe_3)_2]_2$, $[\{(Me_3Si)_2NC(N—\textit{cyclo}\text{-}Hex)_2\}YbI(THF)_2]_2$, and $[\{(Me_3Si)_2N\}Y(THF)(\mu\text{-}Cl)]_2$ complexes

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The insertion of *N*,*N*′-dicyclohexylcarbodiimide at one of the Y—N bonds of the $[(Me_3Si)_2N]_3Y$ complex in toluene at 70 °C afforded the monoguanidinate diamide derivative $\{(Me_3Si)_2NC(N—\textit{cyclo}\text{-}Hex)_2\}Y[N(SiMe)_3]_2$ (**1**) (*cyclo*-Hex is cyclohexyl) in 72% yield. The reaction of equimolar amounts of sodium *N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate, which was prepared *in situ* from $\{(Me_3Si)_2N\}Na$ and *N*,*N*′-dicyclohexylcarbodiimide, and $YbI_2(THF)_2$ in THF gave the $[\{(Me_3Si)_2NC(N—\textit{cyclo}\text{-}Hex)_2\}YbI(THF)_2]_2$ complex (**2**). An attempt to use this procedure for the synthesis of the yttrium compound $\{(Me_3Si)_2NC(NSiMe_3)_2\}_2YCl$ containing the sterically more hindered guanidinate ligand unexpectedly led to the formation of the diamide chloride complex $[\{(Me_3Si)_2N\}_2Y(THF)(\mu\text{-}Cl)]_2$ (**3**). The structures of complexes **1**—**3** were established by X-ray diffraction. Compound **1** is mononuclear. Complexes **2** and **3** are dinuclear and contain two μ^2-bridging halide ligands.

Key words: rare-earth metals, complexes, guanidinate ligand, *N*,*N*-ligand, synthesis, structure, X-ray diffraction study.

Earlier,[1—5] it has been found that sandwich- and half-sandwich-type alkyl and hydride derivatives of rare-earth metals display unique reactivity. These compounds exhibit high activity in catalysis of various transformations of unsaturated substrates.[6—10] Unlike sandwich- and half-sandwich-type rare-earth metal complexes, which have been studied in depth, their analogs having a non-cyclopentadienyl coordination environment remain poorly known.[11—13] Nitrogen-containing ligands are of most interest as hard Lewis acids and also due to valence capacity and coordination capabilities of the nitrogen atoms.[14,15] We used the bulky monoanionic guanidinate ligands, which are electronic analogs of the cyclopentadienyl anion and whose electronic and steric properties can easily be modified[16] by replacing hydrocarbon substituents at the nitrogen atom. Recently, these ligands have been successfully used for the synthesis of new rare-earth metal complexes.[17—20] In the present study, we performed the synthesis of rare-earth metal guanidinate amide and guanidinate halide complexes, which we plan to use as the starting compounds in the synthesis of the corresponding alkyl and hydride derivatives.

Results and Discussion

Two different methods for the insertion of the guanidinate ligand into rare-earth metal complexes are known. One of these methods involves the metathesis reaction of anhydrous rare-earth metal halide with alkali metal guanidinate.[17—21] Another method is based on the insertion of disubstituted carbodiimides at the Ln—N bond giving rise to the guanidinate fragment in the coordination sphere of the metal atom.[22—25]

We found that the reaction of equimolar amounts of $[(Me_3Si)_2N]_3Y$ and *N*,*N*′-dicyclohexylcarbodiimide in toluene at 70 °C led to the insertion of the latter at one of the Y—N bonds of the tris-amide to form the corresponding monoguanidinate diamide complex $\{(Me_3Si)_2NC(N—\textit{cyclo}\text{-}Hex)_2\}Y[N(SiMe)_3]_2$ (**1**) (*cyclo*-Hex is cyclohexyl), which was isolated after recrystallization from hexane in 72% yield (Scheme 1).

The bulky *N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate ligand appeared to be convenient also for stabilization of ytterbium(II) derivatives. We synthesized the mixed-ligand guanidinate iodide complex $[\{(Me_3Si)_2NC(N—\textit{cyclo}\text{-}Hex)_2\}Yb(\mu\text{-}I)(THF)_2]_2$ (**2**) by

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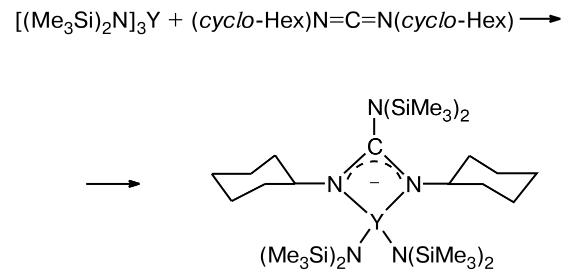
Scheme 1

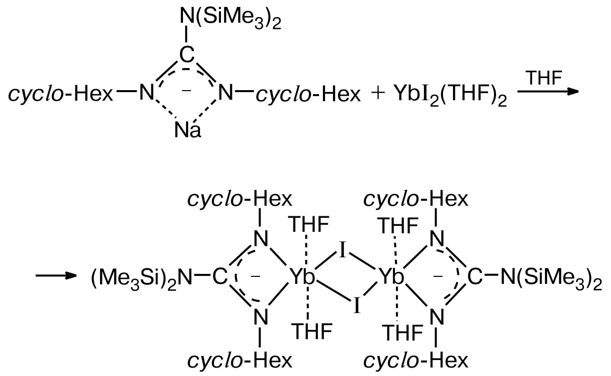


1

i. Toluene, 70 °C.

the metathesis reaction of $YbI_2(THF)_2$ with sodium guanidinate $\{(Me_3Si)_2NC(N—$*cyclo*-$Hex)_2\}Na$ (molar ratio was 1 : 1, 20 °C), which was prepared *in situ* from equimolar amounts of $(Me_3Si)_2NNa$ and *N,N*′-dicyclohexylcarbodiimide in THF (Scheme 2). Compound **2** was isolated after recrystallization from hexane as bright-yellow crystals in 66% yield.

Scheme 2



2

An attempt to use an analogous procedure for the synthesis of an yttrium compound containing the sterically more hindered *N,N*′,*N*″-tris(trimethylsilyl)guanidinate ligand did not lead to the expected result. After the successive addition of *N,N*′-trimethylsilylcarbodiimide and YCl_3 to a solution of lithium amide $(Me_3Si)_2NLi(Et_2O)$ in THF (molar ratio was 2 : 2 : 1, 40 °C) at room temperature, we isolated the diamido chloride complex $\{[(Me_3Si)_2N]_2Y(THF)(\mu\text{-}Cl)\}_2$ (**3**) in 79% yield instead of the expected $\{(Me_3Si)_2NC(NSiMe_3)_2\}YCl$ complex (Scheme 3).

Scheme 3

$$2\,[(Me_3Si)_2N]Li(Et_2O) + 2\,Me_3SiN{=}C{=}NSiMe_3 + YCl_3 \longrightarrow \xrightarrow{\text{THF, 20 °C}} \{[(Me_3Si)_2N]_2Y(THF)(\mu\text{-}Cl)\}_2$$

3

Evidently, the reaction of lithium amide with $Me_3SiN{=}C{=}NSiMe_3$ does not occur under these conditions (THF, 40 °C), although the analogous reaction with (*cyclo*-Hex)N=C=N(*cyclo*-Hex) is completed within 1 h even at room temperature to give the reaction product in 100% yield. Apparently, strong shielding of the conjugated double bond system in *N,N*′-trimethylsilylcarbodiimide by the bulky Me_3Si groups hinders the nucleophilic addition of bis(trimethylsilyl)lithium.

Complexes **1** and **3** were obtained as colorless crystals. Complex **2** is a yellow crystalline compound. Compounds **1—3** are sensitive to atmospheric oxygen and moisture and are readily soluble in ethereal solvents and aromatic and aliphatic hydrocarbons.

The ^1H NMR spectrum of diamagnetic complex **1** (benzene-d_6, 20 °C) shows the following set of signals belonging to the guanidinate ligand: a singlet at δ_H 0.44 assigned to the methyl protons of the $N(SiMe_3)_2$ fragments and a multiplet at δ_H 1.17—1.93 belonging to the methylene protons of the cyclohexyl groups. The methine protons of the cyclohexyl fragments give a complex multiplet at δ_H 3.28. The ^{13}C NMR spectrum shows signals for the carbon atoms of the guanidinate ligand at δ 5.0 ($N(SiMe_3)_2$), 26.0, 26.1, 38.0 (methylene carbon atoms of the cyclohexyl fragments), 55.0 (methine carbon atoms of the cyclohexyl fragments), and 169.3 (quaternary C atom). In the ^1H NMR spectrum, the trimethylsilyl protons of the bis(trimethylsilyl)amide groups give two singlets with equal intensities at δ_H 0.23 and 0.30. In the ^{13}C NMR spectrum, the carbon atoms of these fragments are also characterized by two signals (δ_H 2.6 and 4.1), which is indicative of their magnetic nonequivalence. The ^1H and ^{13}C NMR spectra of complex **2** show sets of signals characteristic of the guanidinate and tetrahydrofuran ligands. 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 colorless crystals of complex **1** suitable for X-ray diffraction study were grown by slow evaporation of a hexane solution at room temperature. X-ray diffraction study demonstrated that complex **1** exists in the crystalline state as two crystallographically independent molecules. The yttrium atom in complex **1** is coordinated by two nitrogen atoms of one bidentate guanidinate ligand and two nitrogen atoms of the bis(trimethylsilyl)amide ligands. The formal coordination number of the Y atom is four, which is a very low value for rare-earth metal complexes[1] (Fig. 1, Table 1).

The chelate guanidinate ligand is coordinated to the central yttrium atom through two Y—N bonds of similar lengths (2.311(1), 2.343(1), 2.327(1), and 2.354(1) Å). The average Y—N bond length (nitrogen atom of the guanidinate fragment) in compound **1** is

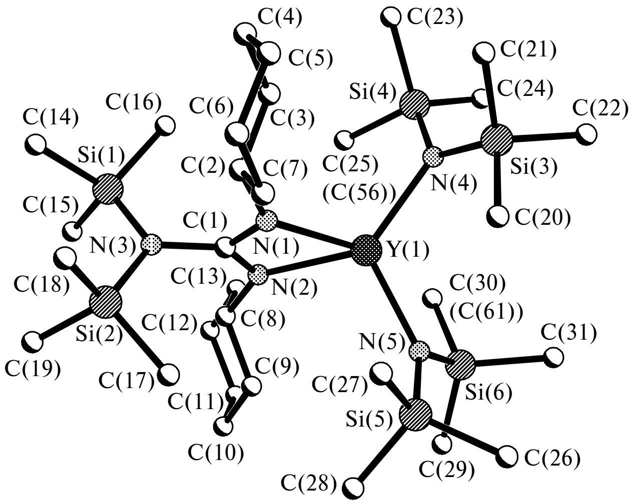


Fig. 1. Structure of the $\{(Me_3Si)_2NC(N\text{—}\mathit{cyclo}\text{-}Hex)_2\}Y[N(SiMe)_3]_2$ complex (**1**). One of two crystallographically independent molecules is shown.

Table 1. Selected bond lengths (d/Å) and bond angles (ω/deg) in complex **1** (in both crystallographically independent molecules **A** and **B**)

A		**B**	
Parameter	Value	Parameter	Value
Bond	d/Å	Bond	d/Å
Y(1)—N(1)	2.311(1)	Y(2)—N(7)	2.327(1)
Y(1)—N(2)	2.343(1)	Y(2)—N(6)	2.354(1)
Y(1)—N(4)	2.252(2)	Y(2)—N(10)	2.255(1)
Y(1)—N(5)	2.235(1)	Y(2)—N(9)	2.226(1)
Si(1)—N(3)	1.767(1)	Si(7)—N(8)	1.768(1)
Si(2)—N(3)	1.768(1)	Si(8)—N(8)	1.765(1)
Si(3)—N(4)	1.718(2)	Si(9)—N(9)	1.719(2)
Si(4)—N(4)	1.711(2)	Si(10)—N(9)	1.709(1)
Si(5)—N(5)	1.720(1)	Si(11)—N(10)	1.727(2)
Si(6)—N(5)	1.713(1)	Si(12)—N(10)	1.713(2)
N(1)—C(1)	1.344(2)	N(6)—C(32)	1.336(2)
N(2)—C(1)	1.333(2)	N(7)—C(32)	1.339(2)
N(3)—C(1)	1.429(2)	N(8)—C(32)	1.434(2)
Angle	ω/deg	Angle	ω/deg
N(2)C(1)N(1)	114.6(1)	N(7)C(32)N(8)	122.7(1)

2.334 Å, which is substantially larger than the Y—N covalent bond lengths in the yttrium complexes $(C_5Me_5)_2YN(SiMe_3)_2$ (2.274 and 2.253 Å)[26] and $[(Me_3Si)_2N]_3Y$ (2.224(6) Å)[27] but is similar to the corresponding distances in the related amidinate complex $[(C_6Me_3H_2)_2C_6H_3C(N\text{-}Pr^i)_2]Y[N(SiMe_3)_2]_2$ (2.34(1) Å).[28] In the NCN fragments coordinated to the metal atom, the N—C bond lengths are almost equal (1.344(2), 1.333(2), 1.336(2), and 1.339(2) Å), which is indicative of the negative charge delocalization. The C(1)—N(3) and C(32)—N(8) distances (1.429(2) and 1.434(2) Å, respectively) are substantially longer than the distances in the NCN fragments due to the fact that this nitrogen atom is not involved in conjugation. The bonds between the yttrium atom and the nitrogen atoms of the bis(trimethylsilyl)amide fragments are in the range of 2.226(1)—2.256(1) Å and are comparable with the distances in the tris-amide $[(Me_3Si)_2N]_3Y$ (2.224(6) Å).[27] The most interesting structural feature of compound **1** is the presence of agostic interactions between the yttrium atom and the carbon atoms of the methyl groups as evidenced by the short Y(1)—C(30) (2.978(2) Å), Y(2)—C(56) (3.050(2) Å), and Y(2)—C(61) (3.044(2) Å) contacts, which are comparable with the distances observed in the $[Y(OC_6H_3Ph_2\text{-}2,6)_3]$ compound (2.84(1)—3.43(1) Å)[29] and are substantially shorter than the other Y—C(Me) distances in **1** (3.251—4.712 Å). The involvement of the C(30), C(56), and C(61) atoms in nonbonded interactions with the yttrium atom leads to an elongation of the corresponding Si—C bonds (Si(6)—C(30), 1.893(2) Å; Si(10)—C(56), 1.892(2) Å; Si(12)—C(61), 1.882(2) Å) compared to the other Si—C(Me) distances (1.853(2)—1.878(2) Å). The presence of agostic interactions in the crystal structure of **1** is confirmed also by the N—Si—C(30, 56, 61) bond angles (106.1(4), 105.8(4), and 106.0(4)°, respectively), which are systematically smaller than the analogous bond angles in the fragments in which this interaction is absent (108.0(1)—115.50(8)°). It should be noted that the Y(1)—C(25) distance (3.251(2) Å) does not lead to an increase in the corresponding Si(4)—C(25) distance (1.858(2) Å), but substantially decreases the N(4)—Si(4)—C(25) bond angle (106.77(9)°). Apparently, changes in the bond angles are more sensitive to agostic interactions than changes in the bond lengths. Earlier, an agostic interaction has been found[30] in sterically hindered silylamides of the metallocene series, $(C_5Me_5)_2YN(SiHMe_2)_2$ and $(C_5Me_4H)_2YN(SiHMe_2)_2$, characterized by analogous changes in the geometry of the environment of the silicon atom. The presence of the agostic interaction in complex **1** may also be responsible for the nonequivalence of the methyl carbon atoms of the bis(trimethylsilyl)amide groups in the ^{13}C NMR spectrum.

Transparent yellow crystals of complex **2** were grown by slow evaporation of its saturated solution in hexane at room temperature.

X-ray diffraction study demonstrated that complex **2** is dinuclear. Two ytterbium atoms are linked to each other by two iodide bridges (Fig. 2, Table 2). The ytterbium atom in complex **2** has a distorted octahedral coordination environment formed by two nitrogen atoms of one bidentante guanidinate ligand, two bridging iodine atoms, and two oxygen atoms of two THF molecules. The Yb—N bond lengths in compound **2** are almost equal to each other (2.408(3) and 2.406(4) Å), are substantially larger

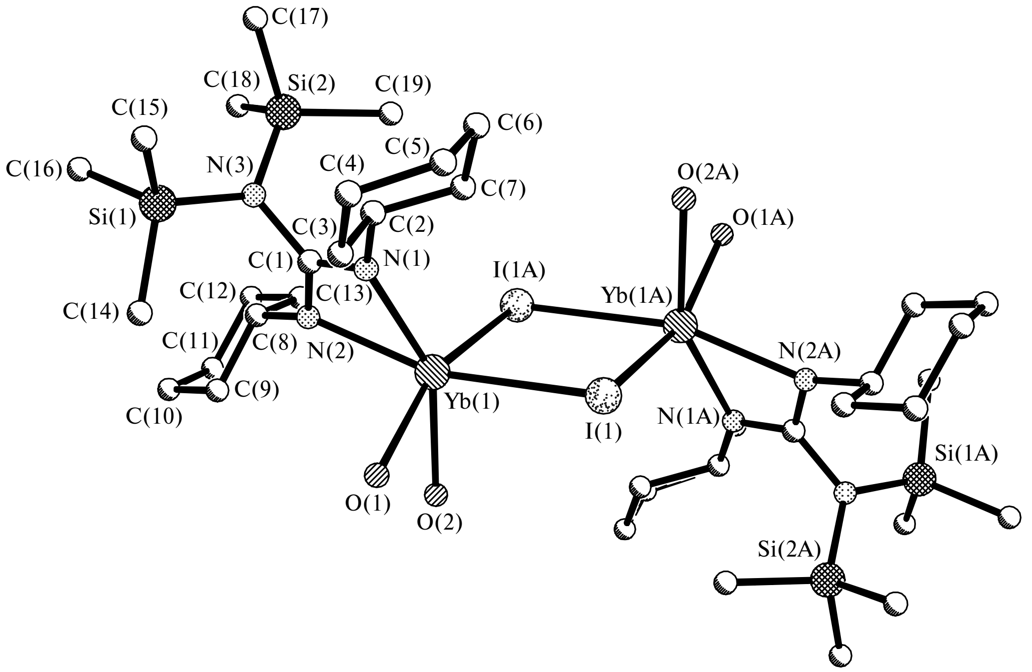


Fig. 2. Structure of the $[\{(Me_3Si)_2NC(N—$*cyclo*-$Hex)_2\}Yb(\mu\text{-}I)(THF)_2]_2$ complex (**2**). The methylene groups of the THF molecules are omitted.

Table 2. Selected bond lengths (*d*/Å) and bond angles (ω/deg) in complex **2**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
Yb(1)—N(1)	2.406(4)	N(1)—C(1)	1.324(5)
Yb(1)—N(2)	2.408(3)	N(2)—C(1)	1.328(5)
Yb(1)—O(1)	2.436(3)	N(3)—C(1)	1.457(5)
Yb(1)—O(2)	2.492(3)	Si(1)—N(3)	1.747(3)
Yb(1)—I(1)	3.1457(3)	Si(2)—N(3)	1.752(3)
Yb(1)—I(1A)	3.2063(4)		
Angle	ω/deg	Angle	ω/deg
I(1)Yb(1)I(1A)	86.907(9)	N(1)C(1)N(2)	116.3(4)
Yb(1)I(1)Yb(1A)	93.093(9)		

than the terminal Yb^{II}—N covalent bond lengths,[31–33] and are comparable with those in β-diketiminate complexes of divalent ytterbium.[34] The Yb—I distances in compound **2** are substantially different (3.1457(3) and 3.2063(4) Å) and are comparable with the bond lengths in the half-sandwich dimers $[(C_5Me_5)Yb(\mu\text{-}I)(THF)_2]_2$ (see Ref. 35) and $[(C_5Me_4SiMe_2NHCMe_3)Yb(\mu\text{-}I)(THF)_2]_2$.[36] In the four-membered metallocycle, the N—C distances are almost equal (1.324(5) and 1.328(5) Å), which is indicative of the presence of conjugation in the guanidinate anion. The N—Yb—N bond angle in this metallocycle is 56.0(1)°. The mutual arrangement of the $N(SiMe_3)_2$ groups and the cyclohexyl substituents of the guanidinate ligands relative to the NCN plane is evidence for their mutual steric repulsion.

Colorless transparent crystals of compound **3** were grown by slow cooling of a toluene solution (Fig. 3, Table 3).

X-ray diffraction study demonstrated that in the crystalline state, complex **3** is dinuclear and contains two bridging chlorine atoms. Simultaneous coordination of the latter to two yttrium atoms gives rise to the planar centrosymmetric four-membered Y_2Cl_2 ring. Compound **3** is isostructural with the $\{[(Me_3Si)_2N]_2Ln(THF)(\mu\text{-}Cl)\}_2$

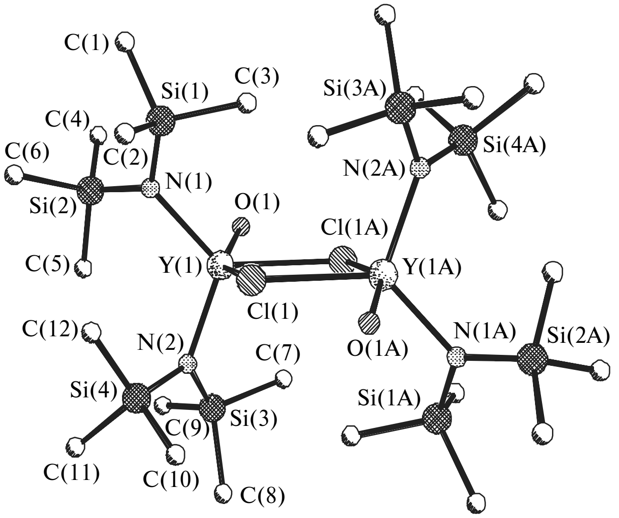


Fig. 3. Structure of the $[\{(Me_3Si)_2N\}_2Y(THF)(\mu\text{-}Cl)]_2$ complex (**3**). The methylene groups of the THF molecules are omitted.

Table 3. Selected bond lengths (d/Å) and bond angles (ω/deg) in complex **3**

Parameter	Value	Parameter	Value
Bond	d/Å	Bond	d/Å
Y(1)—N(1)	2.231(3)	Si(1)—N(1)	1.735(3)
Y(1)—N(2)	2.201(3)	Si(2)—N(1)	1.712(3)
Y(1)—Cl(1)	2.7147(9)	Si(3)—N(2)	1.731(3)
Y(1)—Cl(1A)	2.7137(9)	Si(4)—N(2)	1.730(3)
Y(1)—O(1)	2.380(2)		
Angle	ω/deg	Angle	ω/deg
Cl(1)Y(1)Cl(1A)	74.86(3)	Y(1)Cl(1)Y(1A)	105.14(3)

complexes (Ln = Gd or Yb) prepared earlier.[37] In complex **3**, the coordination environment of the yttrium atom is composed of two nitrogen atoms of two bis(trimethylsilyl)amide ligands, two bridging chlorine atoms, and the oxygen atom of the tetrahydrofuran molecule. Hence, the formal coordination number, 5, is very low. The Y—N bond lengths in complex **3** are substantially different (2.201(3) and 2.231(3) Å) and are comparable with the distances in the tris-amide $[(Me_3Si)_2N]_3Y$ (2.224(6) Å).[27] The Y—Cl bond lengths in molecule **2** are 2.7147(9) and 2.7137(9) Å and are similar to those in the dinuclear complexes $\{[(Me_3Si)_2NC(N^iPr)_2]_2Y(\mu\text{-}Cl)\}_2$ (2.7128(15) and 2.7166(15) Å)[18] and $[Cp_2Y(\mu\text{-}Cl)]_2$ (2.68(1) and 2.69(1) Å)[38] studied earlier.

Therefore, tetrasubstituted guanidinate ligands enable the synthesis of stable derivatives of rare-earth metals in oxidation states +3 and +2. In such compounds, the coordination number of the central metal is low. The insertion of *N*,*N*-disubstituted carbodiimides at the Ln—N bond can be used as a convenient synthetic method for the insertion of the guanidinate fragment into metal complexes.

Experimental

The syntheses were carried out under conditions precluding exposure to atmospheric oxygen and moisture with the use of the standard Schlenk technique. The solvents (THF, hexane, and toluene) were dried over 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 (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 known shifts of the residual protons of deuterated solvents. Anhydrous YCl_3,[39] $(Me_3Si)_2NLi(Et_2O)$,[40] and $[(Me_3Si)_2N]_3Y$ [27] were prepared according to known procedures. *N*,*N*′-Bis(trimethylsilyl)carbodiimide and *N*,*N*′-dicyclohexylcarbodiimide were purchased from Acros. *N*,*N*′-Bis(trimethylsilyl)carbodiimide was used after drying with molecular sieves A4 and vacuum condensation. *N*,*N*′-Dicyclohexylcarbodiimide was used without additional purification.

Yttrium(III) bis(trimethylsilyl)amide [*N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate], $\{(Me_3Si)_2NC(N—\textit{cyclo}\text{-}Hex)_2\}Y[N(SiMe_3)_2]_2$ (1). A solution of *N*,*N*′-dicyclohexylcarbodiimide (0.84 g, 4.06 mmol) in toluene (15 mL) was added to a solution of yttrium tris-amide $[(Me_3Si)_2N]_3Y$ (2.31 g, 4.06 mmol) in toluene (25 mL). The reaction mixture was stirred at 70 °C for 16 h. Toluene was removed *in vacuo* and the solid residue was extracted with hexane (30 mL). After recrystallization from hexane, compound **1** was isolated as colorless crystals in a yield of 2.27 g (72%). Found (%): C, 47.58; H, 10.16; Y, 11.19. $C_{31}H_{76}N_5Si_6Y$. Calculated (%): C, 47.99; H, 9.79; Y, 11.46. ^{1}H NMR (20 °C, benzene-d$_6$), δ: 0.23 (s, 24 H, $YN(SiMe_3)_2$); 0.30 (s, 12 H, $YN(SiMe_3)_2$); 0.44 (s, 18 H, $CN(SiMe_3)_2$); 1.17—1.93 (m, 20 H, $C\underline{H}_2$, cyclohexyl); 3.28 (m, 2 H, $C\underline{H}$, cyclohexyl). ^{13}C NMR (20 °C, benzene-d$_6$), δ: 2.6, 4.1 ($YN(SiMe_3)_2$); 5.0 ($CN(SiMe_3)_2$); 26.0, 26.1, 38.0 ($\underline{C}H_2$, cyclohexyl); 55.0 ($\underline{C}H$, cyclohexyl); 169.3 ($\underline{C}N_3$).

Ytterbium(II) bis[*N*,*N*′-dicyclohexyl-*N*″-bis(trimethylsilyl)guanidinate] tetrahydrofuran iodide (2). A solution of *N*,*N*′-dicyclohexylcarbodiimide (0.57 g, 2.78 mmol) in THF (10 mL) was added to a solution of $(Me_3Si)_2NNa$ (0.51 g, 2.78 mmol) in THF (25 mL) at room temperature. The reaction mixture was stirred for 2 h. Then $YbI_2(THF)_2$ (1.58 g, 2.78 mmol) was slowly added, the reaction mixture was stirred for 12 h and filtered, THF was removed by vacuum condensation, and the solid residue was extracted with hexane. The hexane extracts were filtered and concentrated to 1/4 of the initial volume. After cooling of the solution to –20 °C, a yellow crystalline precipitate was obtained. The crystals were washed with cold hexane and dried *in vacuo* at room temperature. Dark-yellow crystals of **2** were isolated in a yield of 1.47 g (66%). Found (%): C, 30.58; H, 6.61; Yb, 20.89. $C_{54}H_{112}I_2N_6O_4Si_4Yb_2$. Calculated (%): C, 40.01; H, 6.90; Yb, 21.34. ^{1}H NMR (20 °C, benzene-d$_6$), δ: 0.41 (s, 18 H, $CN(SiMe_3)_2$); 0.97—1.90 (m, 28 H, $C\underline{H}_2$ cyclohexyl, β-$C\underline{H}_2$, THF); 3.50 (m, 2 H, $C\underline{H}$, cyclohexyl); 4.19 (s, 8 H, α-$C\underline{H}_2$, THF). ^{13}C NMR (20 °C, benzene-d$_6$), δ: 2.5 ($CN(SiMe_3)_2$); 22.8, 26.1, 38.1 ($\underline{C}H_2$, cyclohexyl); 25.4 (β-$\underline{C}H_2$, THF); 55.2 ($\underline{C}H$, cyclohexyl); 69.7 (α-$\underline{C}H_2$, THF), 169.3 ($\underline{C}N_3$).

Yttrium(III) bis[bis(trimethylsilyl)amide] tetrahydrofuran chloride, $\{[(Me_3Si)_2N]Y(\mu\text{-}Cl)(THF)\}_2$ (3). A solution of bis(trimethylsilyl)carbodiimide (0.93 mL, 0.77 g, 4.14 mmol) in THF (10 mL) was added to a solution of lithium bis(trimethylsilyl)amide $(Me_3Si)_2NLi(Et_2O)$ (0.99 g, 4.14 mmol), in THF (20 mL). The reaction mixture was stirred at 40 °C for 8 h, added to a suspension of YCl_3 (0.41 g, 2.07 mmol) in THF (15 mL), and stirred at 40 °C for 16 h. Then THF was removed by vacuum condensation, and the solid residue was recrystallized from toluene. Colorless crystals of **3** were isolated in a yield of 0.85 g (79%). Found (%): C, 36,84; H, 9,01; Y, 17.06. $C_{32}H_{88}Cl_2N_4O_2Si_8Y_2$. Calculated (%): C, 37.17; H, 8.51; Y, 17.19. ^{1}H NMR (20 °C, benzene-d$_6$), δ: 0.44 (s, 72 H, $YN(SiMe_3)_2$); 1.26 (br.s, 8 H, β-$C\underline{H}_2$, THF); 3.84 (br.s, 8 H, α-$C\underline{H}_2$, THF). ^{13}C NMR (20 °C, benzene-d$_6$), δ: 5.3 ($YN(SiMe_3)_2$); 24.9 (β-$\underline{C}H_2$, THF); 70.5 (α-$\underline{C}H_2$, THF).

X-ray diffraction study. X-ray diffraction data sets were collected on an automated Smart APEX diffractometer (graphite monochromator, Mo-Kα radiation, ω—φ scanning technique, the exposure time was 10 s per frame) at 100 K for complexes **1** and **3** and at 168 K for complex **2**.

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 complexes **1** (except for the hydrogen atoms at C(21)) and **3**

Table 4. Crystallographic parameters of complexes **1**, **2**, and **3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{31}H_{76}N_5Si_6Y$	$C_{54}H_{112}I_2N_6O_4Si_4Yb_2 \cdot C_6H_{14}$	$C_{32}H_{88}Cl_2N_4O_2Si_8Y_2$
Molecular weight	776.4	1707.9	1034.50
Space group	$P2(1)/c$	$C2/c$	$P2(1)/n$
a/Å	18.704(2)	33.184(1)	14.128(1)
b/Å	24.065(3)	9.7163(4)	12.975(1)
c/Å	20.134(3)	24.587(1)	16.372(2)
β/deg	90.755(3)	106.744(1)	114.520(2)
V/A^3	9062(2)	7591.4(5)	2730.4(4)
Z	8	4	2
ρ_{calc}/g cm^{-3}	1.138	1.494	1.258
μ/mm^{-1}	1.471	3.37	2.417
Scan range, θ/deg	29.05	28	25
Number of measured reflections	66022	36860	14573
Number of reflections with $I > 2\sigma$	23926	9148	4806
R_{int}	0.0487	0.0822	0.0595
Number of parameters in refinement	1371	343	402
GOOF (F^2)	0.968	0.965	0.978
R_1 ($I > 2\sigma(I)$)	0.0414	0.0477	0.0373
wR_2 (all data)	0.0994	0.1007	0.0834
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	0.834/–0.465	1.488/–0.668	0.691/–0.513

were located from difference electron density maps and refined isotropically. All H atoms in complex **2** and the H atoms at C(21) in molecule **1** were placed in geometrically calculated positions and refined using a riding model. In complex **2**, a hexane molecule of solvation was revealed and refined isotropically. The hydrogen atoms in this molecule were not located.

All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[41] Absorption corrections were applied using the SADABS program.[42] Principal crystallographic characteristics and details of X-ray diffraction study are given in Table 4.

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