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# Synthesis and structure of samarium benzyl complex supported by bridged bis(guanidinate) ligand and its reactivity toward nitriles and phenyl isocyanate

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#### A R T I C L E I N F O

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# ABSTRACT

Reaction of SmCl<sub>3</sub> with one equivalent of LLi<sub>2</sub> (L = *i*Pr(Me<sub>3</sub>Si)NC(NiPr)N(CH<sub>2</sub>)<sub>3</sub>NC(NiPr)N(SiMe<sub>3</sub>)*i*Pr) in THF afforded monochloride complex LSmCl(THF)<sub>2</sub> (**1**) or LSmCl(DME) (**2**) upon crystallization from THF or DME. Treatment of **1** with KCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> yielded monobenzyl complex LSm( $\eta^1$ -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(DME) (**3**). The reactivity of **3** has been further studied with MeCN, 4-MeOC<sub>6</sub>H<sub>4</sub>CN and PhNCO. Complex **3** reacts with MeCN to produce [LSm( $\mu$ -(*N*,*N'*)-N(H)C(Me)=C(H)C=N)(THF)]<sub>2</sub> (**4**) via metalation of the methyl group of MeCN and followed by insertion of another MeCN into the new Sm–C bond and 1,3-H shift. Insertion into Sm–benzyl of **3** occurs with 4-MeOC<sub>6</sub>H<sub>4</sub>CN to form a dimeric complex [LSm( $\mu$ -NH(C<sub>6</sub>H<sub>5</sub>(*p*-OMe))) (**C**=CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SmL] (**5**) with a new group NH(C<sub>6</sub>H<sub>5</sub>(*p*-OMe))C=CC<sub>6</sub>H<sub>5</sub> in a  $\eta^3$ -1-aza-allyl coordination mode via 1,3-H shift. Complex **3** reacts with PhNCO to yield a double insertion dinuclear complex [L'Sm{ $\mu$ -OC(CH<sub>2</sub>Ph)N(Ph)}<sub>2</sub>SmL'] (**6**) (L' = *i*Pr(Me<sub>3</sub>Si)NC(N *i*Pr)N(CH<sub>2</sub>)<sub>3</sub>(SiMe<sub>3</sub>)C(N*i*Pr)<sub>2</sub>(CN(Ph)O)) via insertion reactions of PhNCO both into Sm–benzyl and into Sm–guanidinate of L followed by the rearrangement of the newly formed bridged ligand L'. Complexes **1**–**6** were fully characterized including X-ray structure analyses.

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# 1. Introduction

Guanidinate anions, as one of the alternatives to cyclopentadienyl anions, have attracted increasing attention in organolanthanide chemistry since they have the advantages of tunable steric and electronic effects by variation of the substituents on the nitrogen atoms and varied binding modes arisen from the third nitrogen chelating ability [1–6]. A wide range of organolanthanide derivatives stabilized by guanidinate ligands have been synthesized and proven to be potential as efficient catalysts in homogenous catalyzes [7–17], and as photoelectric materials [18] and the precursors for ALD and MOCVD processes [19–22].

In contrast, the application of bridged guanidinate ligands in lanthanide chemistry still remains unexplored, although these ligands can prevent ligand redistribution reactions and provide the metal center with rigid framework and more open coordination sphere, which are useful in homogeneous catalysis.

Recently, we have reported that bis(amidinate) ligand can provide a suitable coordination environment for stabilizing lanthanide amides [23], alkoxides [24] and monoborohydrides [25]. All these complexes can serve as highly active single-site initiators

0022-328X/\$ – see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2012.06.004 for ring-open-polymerization of cyclic esters and the amide complexes are active for catalytic addition of amines to nitriles selectively to monosubstituted amidines [26]. Guanidinate and amidinate groups possess similar coordination and chemical properties. To expand our research on the lanthanide chemistry with bridged noncyclopentadienyl ligands, we tried to synthesize lanthanide benzyl complex bearing the bridged guanidinate L (L = *i*Pr(Me<sub>3</sub>Si)NC(N*i*Pr)N(CH<sub>2</sub>)<sub>3</sub>NC(N*i*Pr)N(SiMe<sub>3</sub>)*i*Pr). Here we would like to report the detailed syntheses and molecular structures of samarium monochloride complexes LSmCl(THF)<sub>2</sub> (**1**) and LSmCl(DME) (**2**) and benzyl complex LSm( $\eta^{1}$ -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(DME) (**3**) and the reactivity of **3** toward benzonitrile, acetonitrile and phenyl isocyanate.

### 2. Results and discussion

2.1. Syntheses and characterization of  $LSmCl(THF)_2$  (**1**) and LSmCl(DME) (**2**) ( $L = iPr(Me_3Si)NC(NiPr)N(CH_2)_3NC(NiPr)N(SiMe_3)$  iPr)

Reaction of anhydrous SmCl<sub>3</sub> with one equivalent of lithium salt LLi<sub>2</sub>, which was formed in situ by treatment of Li<sub>2</sub>(Me<sub>3-</sub>SiN(CH<sub>2</sub>)<sub>3</sub>NSiMe<sub>3</sub>) with two equivalents of N,N'-diisopropylcarbodiimide in THF at room temperature for 24 h, afforded the monochloride complex LSmCl(THF)<sub>2</sub> (**1**) upon crystallization from

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a mixture of THF/hexane, or LSmCl(DME) (**2**) from DME solution (Scheme 1).

Complexes **1** and **2** were fully characterized by elemental analyses, IR and X-ray single-crystal structure determinations. Their molecular structures are shown in Figs. 1 and 2, respectively, and the selected bond lengths and angles are listed in Table 1.

Complexes **1** and **2** both adopt a monomeric structure in their solid state. The central metal Sm in each complex is ligated by two guanidinate moieties of one ligand L through four nitrogen atoms, one chlorine atom, and two oxygen atoms to form a distorted trigonal bipyramid, if the guanidinate ligands are considered to be point donors located at the central carbon.

The nearly identical C–N lengths within the chelating guanidinate ligands (1.311(8) Å–1.325(8) Å) suggest that the  $\pi$ -electrons within the NCN fragments are delocalized. The average Sm–N distance for the guanidinate nitrogen atoms attached to the bridge is about 0.10 Å shorter than that for those attached to the –*i*Pr groups. Whilst, almost the same average Ln–N distance for the two guanidinate groups in the complexes bearing unbridged guanidinate ligands were reported [27]. The only difference between **1** and **2** is that the two oxygen atoms are from the coordinated THF molecules for **1** and from one DME molecule for **2**.

# 2.2. Synthesis and characterization of $LSm(\eta^1-CH_2C_6H_5)(DME)$ (3)

With the monochloride **1** in hand the reaction of **1** with one equivalent of KCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> in THF was conducted at 0 °C in an attempt to synthesize the corresponding benzyl complex, as lanthanide benzyl complexes can not only serve as catalysts for hydro-amination/cyclization of aminoalkenes [28], dimerization of phenylacetylenes [29] and activate unsaturated molecules [30,31], but also serve as efficient initiators for polymerization of olefins [32–35]. The reaction took place smoothly and the color of the solution changed from light yellow to deep yellow. After workup, the DME-solvated benzyl complex LSm( $\eta^1$ -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(DME) (**3**) was isolated as yellow crystals in 58% yield (Scheme 2).

Complex **3** is very sensitive to air and moisture. It is well soluble in THF and toluene and moderately soluble in hexane. Elemental analysis of **3** is consistent with its formula. The structure of **3** was further confirmed by an X-ray crystal structure analysis.

Complex **3** crystallizes in a triclinic system with space group  $P\overline{1}$ . The molecular structure of **3** is shown in Fig. 3 and the selected bond lengths and angles are listed in Table 2. Complex **3** adopts a monomeric structure in which the coordination sphere around the Sm atom is composed of four nitrogen atoms of the ligand L, one carbon atom of the benzyl group and two oxygen atoms of the DME molecule. The benzyl ligand adopts an  $\eta^1$ -coordination mode. The bond angle of C(25)–C(24)–Sm(1) is 136.8(7)°, which is comparable with that in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm( $\eta^1$ -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)(THF) [36] but much larger than those found in the complexes with a  $\eta^3$ - or a  $\eta^2$ -benzyl group: {(Me<sub>3</sub>Si)<sub>2</sub>NC(NCy)<sub>2</sub>)<sub>2</sub>Ln( $\eta^3$ -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) (Cy = C<sub>6</sub>H<sub>11</sub>) [37] and {HC-(MeCNAr)<sub>2</sub>}La( $\eta^2$ -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(THF) (Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [38]. The distance of Sm(1)···C(25) is 3.687(8) Å, indicative of no interaction between Sm(1) and C(25). The bond length of Sm(1)–C(24) (2.510(12) Å) is comparable with those found in the benzyl complexes reported previously [39]. The bond parameters in the unit of LSm are comparable well with those in **1** and **2**.

#### 2.3. Reaction of **3** with acetonitrile ( $CH_3CN$ )

The reactivity of lanthanide complexes toward nitriles is of interest, as nitriles constitute another class of unsaturated substrates. Two reaction pathways for the reaction of lanthanide alkyl complexes with acetonitrile have been reported. One is the insertion of acetonitrile into an Ln–alkyl species affording the azomethine insertion complexes [40]. The other one is the C–H activation of an acetonitrile, followed by insertion reaction of the second coordinated acetonitrile into the newly formed Ln–alkyl species [41,42].

To assess the chemical behavior of **3** with nitriles the reaction of **3** with acetonitrile was first tested. Treatment of **3** with two equivalents of acetonitrile resulted in an instantaneous reaction. After workup, pale yellow crystals were isolated in 64% yield. The crystals were fully characterized including an X-ray crystal structure analysis proven to be the crotononitrileamido complex  $[LSm(\mu-(N,N')-N(H)C(Me)=C(H)C=N) (THF)]_2$  (**4**) (Scheme 3).

The IR spectrum shows the strong absorption at 3415 and 2187 cm<sup>-1</sup> which can be assigned to N–H and C=N stretching vibrations, respectively.

The molecular structure of **4** is shown in Fig. 4, and selected bond distances and angles are given in Table 3. Complex **4** crystallizes in a triclinic system with space group  $P\overline{1}$ .

Complex **4** has a centrosymmetric dimeric structure in which the two units of LSm connected together by two crotononitrileamido fragments  $\mu$ -(*N*,*N'*)-N(H)C(Me)=C(H)C=N. Each samarium atom displays a distorted pentagonal bipyramid formed by the ligand L,



Scheme 1. Syntheses of complexes 1 and 2.



**Fig. 1.** ORTEP diagram of the molecular structure of complex **1**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and the free THF molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1 - x + 1, y, -z + 1/2.

two nitrogen atoms from the newly formed crotononitrileamido ligand and one oxygen atom of a THF molecule. The four nitrogen atoms (N(1), N(2), N(3) and N(4)) from the ligand L and N(7A) atom from the nitrile (C $\equiv$ N) group occupy equatorial positions, while oxygen atom O(1) and N(8) site at axial positions with the O(1)– Sm(1)–N(8) angle of 158.7(3)°.

The average Sm–N distance for the guanidinate nitrogen atoms attached to the bridge is about 0.13 Å shorter than those attached to the *i*Pr groups. The bond length of C(27)–N(7) is 1.155(11) Å, in the range of the C $\equiv$ N triple bond, and which is comparable with that found in [{Me<sub>2</sub>Si(NCMe<sub>3</sub>)(OCMe<sub>3</sub>)}<sub>2</sub>Y( $\mu$ -(N,N')-N(H)C(Me) $\equiv$ C(H) C $\equiv$ N)]<sub>2</sub> [41]. The shorter N(8)–C(25) (1.301(12) Å) and C(26)–C(27) (1.378(13) Å) distances and the longer C(25)–C(26) (1.388(14) Å) bond indicate considerable charge delocalization within the crotononitrileamido fragment. The same situation was also found in [{Me<sub>2</sub>Si(NCMe<sub>3</sub>)(OCMe<sub>3</sub>)}<sub>2</sub>Y( $\mu$ -(N,N')-N(H)C(Me) $\equiv$ C(H)C $\equiv$ N)]<sub>2</sub> [41].

It is likely that **4** was formed via the following steps as proposed previously [41]. The C–H bond activation of acetonitrile by **3** 



**Fig. 2.** ORTEP diagram of the molecular structure of complex **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

afforded the intermediate  $[LSm(\mu-(C,N)-CH_2C\equiv N)]_2$ ; The intermediate further reacted with another acetonitrile molecule to give **4** via insertion of acetonitrile followed by a 1,3-H shift.

# 2.4. Reaction of **3** with 4-methoxybenzonitrile (4-MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ N)

Two examples concerning the reactivity of lanthanide alkyl complexes to benzonitriles have been found in the literature till now. The reaction of  $(C_5Me_5)$ ScMe with two equivalents of 4-MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ N afforded a  $\beta$ -diketiminate complex via an attacking of the second coordinated nitrile and a second 1,3-H shift [43]. Whilst, the reaction of  $(C_5Me_5)$ YCH<sub>2</sub>(3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C $\equiv$ N yielded the complex  $(\eta^5-C_5Me_5)_2$ Y[ $\eta^2$ -C{CH<sub>2</sub>(3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)] $\equiv$ N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)](THF) formed via the insertion of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>C $\equiv$ N into the Y–C bond [31].

Thus, the reaction of **3** with 4-MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ N was then conducted. Addition of one equivalent of 4-MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ N into a *n*-hexane solution of **3** at room temperature led to the formation of the new samarium complex [LSm{ $\mu$ -NH(C<sub>6</sub>H<sub>5</sub>(p-OMe))) C=C(C<sub>6</sub>H<sub>5</sub>)]<sub>2</sub>SmL] (**5**) in 59% yield upon crystallization from hexane solution (Scheme 4).

The elemental analysis and IR spectroscopy of complex **5** are in good agreement with the proposed structure. The IR spectrum

able 1	
elected bond lengths (Å) and angles (°) for complexes <b>1</b> and <b>2</b> .	

		-			
Bond lengths	1	2	Bond angles	1	2
Sm(1)-N(1)	2.385 (5)	2.484 (15)	O(1)-Sm(1)-O(1A)	171.2 (2)	_
Sm(1)-N(2)	2.480 (6)	2.355 (15)	N(2)-Sm(1)-N(2A)	179.3 (2)	_
Sm(1)-C(1)	2.878 (5)	2.846 (18)	N(2)-Sm(1)-N(1)	54.1 (7)	54.5 (5)
Sm(1)-O(1)	2.447 (5)	2.514 (13)	N(1)-Sm(1)-N(3)	-	172.5 (6)
Sm(1)-Cl(1)	2.722 (3)	2.653 (5)	O(2)-Sm(1)-Cl(1)	-	160.1 (4)
N(1)-C(1)	1.325 (8)	1.32 (3)	N(2)-C(1)-N(1)	114.4 (5)	114.9 (17)
N(2)-C(1)	1.311 (8)	1.31 (2)			



Fig. 3. ORTEP diagram of the molecular structure of complex 3. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

shows a strong absorption at 3415  $\rm cm^{-1}$  indicative of the presence of N–H bond, which should be formed via 1,3-H shift.

The confirmation of **5** was further made by an X-ray structure analysis. The molecular structure of **5** is shown in Fig. 5 and the selected bond lengths and angles were listed in Table 4. Complex **5** is an unsolvated dimeric structure, in which the two monomers LSmNH( $C_6H_5(p-OMe)$ )C=C( $C_6H_5$ ) were linked by two nitrogen bridges (N(13) and N(14)).

The most interesting structure feature of **5** is that the group  $NH(C_6H_5(p-OMe))C=C(C_6H_5)$  adopts a  $\eta^3$ -1-azaallyl coordination

Table 2	
Selected bond	lengths (Å) and angles (°) for complex <b>3</b> .

Bond distances (Å)			
Sm(1)-N(1)	2.501 (8)	Sm(1)-N(2)	2.384 (8)
Sm(1)-N(3)	2.527 (8)	Sm(1)-N(4)	2.370 (7)
Sm(1)-C(1)	2.868 (9)	Sm(1)-C(2)	2.905 (8)
Sm(1)-C(24)	2.510 (12)	$Sm(1)\cdots C(25)$	3.687 (8)
N(1)-C(1)	1.309 (13)	N(2)-C(1)	1.319 (12)
N(3)-C(2)	1.304 (11)	N(4) - C(2)	1.335 (12)
Bond angles (°)			
N(1)-Sm(1)-N(2)	53.9(3)	N(3)-Sm(1)-N(4)	53.5(3)
N(1)-Sm(1)-C(24)	96.5(4)	O(2) - Sm(1) - C(24)	161.2(9)
N(1)-Sm(1)-N(3)	171.4(3)	C(25)-C(24)-Sm(1)	136.8(7)
N(1)-C(1)-N(2)	114.9(9)		

mode by 1,3-H shift as confirmed by the bond parameters. The bond lengths of C(54)–C(47) (1.379(19) Å) and C(62)–C(69) (1.366(19) Å) are longer than the corresponding C=C double bond and the bond lengths of N(13)–C(54) (1.390(15) Å) and N(14)–C(69) (1.402(18) Å) are shorter than that for the N–C single bond. The bond angles of N(13)–Sm(1)–C(47) and N(14)–Sm(2)–C(62) are 50.8(4)° and 50.0(4)°, respectively. The bond lengths of Sm(1)–C(47) (2.943(13)°Å), Sm(2)–C(54) (2.863(14)°Å), Sm(2)–C(62) (2.954(17)°Å) and Sm(2)–C(69) (2.904(17)°Å) also indicate the presence of the interactions between Sm atoms and these carbon atoms.

The bond lengths of Sm(1)–N(13) and Sm(1)–N(14) are 2.485(12)°Å and 2.554(10)°Å, respectively, which indicate the two nitrogen atoms unsymmetrically coordinated to the samarium atom. Two samarium atoms (Sm(1) and Sm(2)) and two nitrogen atoms (N(13) and N(14)) are nearly coplanar with the sum angles of 360.1(6)° (N(13)–Sm(1)–N(14) 74.4(4)°, Sm(1)–N(13)–Sm(2) 106.2(4)°, N(13)–Sm(2)–N(14) 105.1(4) and N(13)–Sm(1)–N(14) 74.3(4)°).

The average bond length in the two guanidinate units of the ligand L are well comparable with each other, which is different from that found in complexes **1–3**. The difference in bond parameters among them may be attributed to the steric demanding resulted from the presence of the bulky  $NH(C_6H_5(p-OMe)C = CC_6H_5)$  group in **5**.



Scheme 3. Reaction of 3 with acetonitrile.



**Fig. 4.** ORTEP diagram of the molecular structure of complex **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and free hexanes molecules in the lattice are omitted for clarity (Symmetry transformations used to generate equivalent atoms: #1 - x + 1, y, -z + 1/2. #1 - x + 2, -y + 1, -z #2 - x + 1, -y + 1, -z + 1).

# 2.5. Reaction of 3 with phenyl isocyanate (PhNCO)

Table 2

The reactive chemistry of organolanthanide complexes with isocyanates is of interest as isocyanates are not only the useful reagents in organic synthesis, but also important monomers in polymerization chemistry [44–48]. The reaction of lanthanide

Selected bond lengths (Å) and angles (°) for complex <b>4</b> .					
Bond distances (Å)					
Sm(1)-N(1)	2.495 (8)	Sm(1)-C(1)	2.869 (9)		
Sm(1)-N(2)	2.373 (7)	Sm(1)-C(2)	2.885 (8)		
Sm(1)–N(3)	2.501 (8)	N(1)-C(1)	1.312 (12)		
Sm(1)-N(4)	2.383 (7)	N(2) - C(1)	1.321 (12)		
Sm(1)-N(7A)	2.576 (8)	N(3)-C(2)	1.316 (11)		
N(7)-Sm(1A)	2.576 (8)	N(4) - C(2)	1.315 (11)		
Sm(1)-N(8)	2.428 (8)	N(8)-C(25)	1.301 (12)		
C(26)-C(27)	1.378 (13)	C(25)-C(26)	1.388 (14)		
Bond angles (°)					
N(2)-Sm(1)-N(4)	73.0 (2)	N(2)-Sm(1)-N(1)	54.2 (2)		
N(2)-Sm(1)-N(8)	105.2 (3)	N(4) - Sm(1) - N(1)	126.8 (3)		
N(4) - Sm(1) - O(1)	91.4 (3)	O(1) - Sm(1) - N(1)	84.5 (3)		
N(8)-Sm(1)-O(1)	158.7 (3)	N(1)-Sm(1)-N(3)	169.0 (3)		
N(1)-C(1)-N(2)	115.1 (8)	N(4)-C(2)-N(3)	114.7 (7)		

amide complexes with PhNCO afforded the monoinsertion or diinsertion products depending on the amide complexes used [49–55]. The reactions of  $(MeC_5H_4)_2Ln(^nBu)$  and  $(C_5Me_5)_3Ln$  with PhNCO afforded the monoinsertion and diinsertion complexes, respectively [45,46]. In 2009, Zhou's group reported the insertion reaction of PhNCO into the Ln–N bond of a  $\eta^1$ -guanidinate group in complex  $[(C_5H_5)_2Y(\mu-\eta^1:\eta^3-N=C(NMe_2)_2)]_2$  [56]. Thus, the reactivity of **3** with PhNCO should be of interest, as the potential two active groups of Ln-benzyl and Ln-guanidinate are existent in 3. To see whether the two active species both can react with PhNCO molecules, the reaction of 3 with two equivalents of PhNCO was tested in hexane at room temperature. The reaction went smoothly. After workup, colorless crystals were obtained in 61% yield (Scheme 5). Elemental analysis of the crystals is consistent with the formula of a double insertion product, and IR spectrum showed the presence of O----C----N groups. X-ray structural analysis of the crystals showed they are the double insertion complex  $[L'Sm{\mu-}$  $OC(CH_2Ph)N(Ph)$ <sub>2</sub>SmL'] (6) (L' =  $iPr(Me_3Si)NC(NiPr)N(CH_2)_3$ (SiMe<sub>3</sub>)C(NiPr)<sub>2</sub>(CN(Ph)O)). Clearly, complex 6 is formed via insertion reaction of PhNCO into the Sm-C bond and the insertion of the another PhNCO molecule into the Sm-guanidinate group followed by the 1,3-migration of a SiMe<sub>3</sub> group and the rearrangement of the newly formed bridged ligand L'. The occurrence of the ligand



Scheme 4. Reaction of 3 with 4-methoxybenzonitrile.

rearrangement should be attributed to the overcrowded coordination environment around the Sm atoms in the original state.

The molecular structure of **6** is shown in Fig. 6 and the selected bond lengths and angles are given in Table 5. Complex **6** is a solvent-free dinuclear complex containing two newly bridged ligand L' and two O---C(CH<sub>2</sub>Ph)---N(Ph) ligands.

Each central metal is coordinated by one guanidinate and two O=--C(CH<sub>2</sub>Ph)=--N(Ph) ligands in bidentate fashion. The coordination geometry around each Sm atom can be viewed as a capped octahedron. The two oxygen atoms are unsymmetrically coordinated to the samarium atom with the bond lengths of Sm–O being 2.482(4) Å for Sm(1)–O(2) and 2.387(4) Å for Sm(1)–O(2A) Å. The bond lengths of N(7)–C(24), O(1)–C(24), N(8)–C(31) and O(2)–C(31) are 1.319(8) Å, 1.295(7) Å, 1.289(9) Å and 1.317(7) Å, respectively, which are intermediate between a corresponding double-bond distance (N=C, 1.26 Å; C=O, 1.20–1.22 Å) and a single-bond distance (N–C, 1.51 Å; C–O, 1.43 Å), indicative of electron delocalization within the newly formed O–C–N units. The



**Fig. 5.** ORTEP diagram of the molecular structure of complex **5.** Thermal ellipsoids are drawn at the 30% probability level. The SiMe<sub>3</sub> and *i*Pr fragments at N(5), N(6), N(11) and N(12) are omitted for clarity. Hydrogen atoms of carbon atoms and free THF molecule in the lattice are omitted.

observed Sm(1)–N(7A) (2.485(6) Å) and Sm(1)–N(8) (2.541(5) Å) bond lengths are comparable well to those in complexes  $[(MeC_5H_4)_2Ln(\mu,\eta^3-(OC(SPh)NPh))]_2$  [57] and  $\{(MeC_5H_4)_2Ln(THF) [O=-CN(iPr)_2=-NPh]\}$  [49].

The bond angles around C(2) atom is 360°, which is consistent with  $sp^2$  hybridization. The three C–N bond lengths of guanidine group (C(2)–N(6) 1.279(8) Å, C(2)–N(3) 1.433(8) Å and C(2)–N(4) 1.392(8) Å) indicate that the  $\pi$  electron of C—N double bond is not delocalized within the NCN unit.

The possible mechanism for the formation of **6** is presented in Scheme 6. The insertion of PhNCO into Ln-benzyl affords the monoinsertion intermediate **A**. The coordination of the second PhNCO molecule to Sm atom in **A** results in the change of the bonding mode of one guanidinate ligand from  $\eta^3$  to  $\eta^1$  fashion (**B**). The insertion of the second coordinated PhNCO into the Sm- $\eta^1$ -guandinate bond followed by the 1,3-migration of SiMe<sub>3</sub> group and the rearrangement of the L ligand leads to the formation of **6**.

# 3. Experimental section

#### 3.1. *General considerations*

All manipulations were performed under purified argon or nitrogen atmosphere using standard Schlenk techniques and

Table 4	
Selected bond distances (Å) and	angles (°) for complex 5.

Bond distances (Å)			
Sm(1)-N(1)	2.412 (11)	N(3)-C(2)	1.344 (18)
Sm(1)-N(2)	2.430 (11)	N(4)-C(2)	1.314 (19)
Sm(1)-N(3)	2.415 (14)	N(5)-C(1)	1.458 (18)
Sm(1)–N(4)	2.364 (12)	N(6)-C(2)	1.461 (19)
Sm(2)–N(7)	2.448 (12)	N(7)-C(24)	1.334 (18)
Sm(2)–N(8)	2.358 (11)	N(8)-C(24)	1.331 (17)
Sm(2)–N(9)	2.409 (14)	N(9)-C(25)	1.331 (17)
Sm(2)–N(10)	2.440 (11)	Sm(2)–C(69)	2.904 (17)
Sm(1)-C(1)	2.837 (15)	N(1)-C(1)	1.304 (18)
Sm(1)-C(2)	2.838 (16)	N(2)-C(1)	1.335 (18)
Sm(2)–C(24)	2.850 (13)	N(10)-C(25)	1.31 (2)
Sm(2)-C(25)	2.820 (16)	N(14)-C(69)	1.402 (18)
Sm(1)–N(13)	2.485 (12)	N(13)-C(54)	1.390 (15)
Sm(1)–N(14)	2.554 (10)	C(62)-C(69)	1.366 (19)
Sm(2)–N(13)	2.538 (10)	C(47) - C(54)	1.379 (19)
Sm(2)–N(14)	2.507 (12)	C(47)-C(48)	1.482 (18)
Sm(1)–C(47)	2.943 (13)	C(54)-C(55)	1.507 (19)
Sm(1)–C(54)	2.860 (14)	C(62)-C(63)	1.48 (2)
Sm(2)–C(62)	2.954 (17)	C(69)-C(70)	1.49 (2)
Bond angles (°)			
N(1)-Sm(1)-N(2)	54.9 (4)	N(14)-Sm(2)-N(13)	74.3 (4)
N(4) - Sm(1) - N(3)	55.2 (4)	N(13)-Sm(1)-N(14)	74.4 (4)
N(8)-Sm(2)-N(7)	55.3 (4)	Sm(2)-N(14)-Sm(1)	105.1 (4)
N(9)-Sm(2)-N(10)	54.9 (4)	Sm(1)-N(13)-Sm(2)	106.2 (4)
N(1)-Sm(1)-N(3)	112.1 (5)	N(9)-Sm(2)-N(7)	108.4 (5)
N(13)-Sm(1)-C(47)	50.8 (4)	N(14)-Sm(2)-C(62)	50.0 (4)



Scheme 5. Reaction of 3 with phenyl isocyanate.

a glovebox. Tetrahydrofuran, toluene, DME and *n*-hexane were dried and distilled from sodium benzophenone ketal under argon prior to use. The other reagents were purchased from Acros Chemical and used as received without further purification. Me<sub>3</sub>Si(H)N(CH<sub>2</sub>)<sub>3</sub>N(H)SiMe<sub>3</sub> was prepared according to the literature method [58]. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument. Lanthanide analyses were performed by ethylenediaminetetraacetic acid (EDTA) titration with a xylenol orange indicator and a hexamine buffer [59]. The IR spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets.

# 3.2. Synthesis of LLi<sub>2</sub>(THF)

A solution of Me<sub>3</sub>Si(H)N(CH<sub>2</sub>)<sub>3</sub>N(H)SiMe<sub>3</sub> (4.6 g, 21.1 mmol in 40 mL THF) was cooled at 0 °C, *n*-BuLi (17.6 mL, 42.2 mmol, 2.40 M in hexane) was added dropwise, and stirred for 2 h then slowly warmed to room temperature. To this solution was added *N*,*N*'-diisopropylcarbodiimide (*i*PrN=C=N*i*Pr) (6.6 mL, 42.2 mmol) at



**Fig. 6.** ORTEP diagram of the molecular structure of complex **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and methyl groups of SiMe<sub>3</sub> are omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1 - x, -y + 2, -z + 1.

0 °C, then stirred for 2 h. The resulting solution was slowly warmed to room temperature. The THF solvent was removed in vacuo. The remaining crystalline solid was washed with hexane three times and dried to give 11.1 g (95% yield) of the title compound LLi<sub>2</sub>(THF). C<sub>27</sub>H<sub>60</sub>Li<sub>2</sub>N<sub>6</sub>OSi<sub>2</sub> (554.86) calcd.: C, 58.45; H, 10.90; N, 15.15. Found: C, 58.85; H, 11.03; N, 14.79. IR (KBr, cm<sup>-1</sup>): 2971 (s), 2875 (m), 1625 (s), 1528 (m), 1384 (s), 1131 (m), 1016 (m), 843 (w), 593 (w). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 3.87 (m, 2 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.57 (m, 4 H, α-CH<sub>2</sub>, THF), 3.41 (m, 6 H, -CH(CH<sub>3</sub>)<sub>2</sub> and -NCH<sub>2</sub>), 1.85 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.40 (m, 4 H, β-CH<sub>2</sub>, THF), 1.34–1.12 (m, 24 H, -CH<sub>3</sub>), 0.28 (m, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 170.36 (C=N), 67.90 (α-CH<sub>2</sub>, THF), 49.48 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 48.60 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 46.20 (-CH(CH<sub>3</sub>)<sub>2</sub>), 35.00 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 25.60, (β-CH<sub>2</sub>, THF), 24.47 (-CH<sub>3</sub>), 3.04 (-Si(CH<sub>3</sub>)<sub>3</sub>).

# 3.3. Synthesis of LSmCl(THF)<sub>2</sub> (1)

A stirred pale yellow suspension of SmCl<sub>3</sub> (1.10 g, 4.3 mmol) in 20 mL THF was added to a freshly prepared THF solution of LLi<sub>2</sub> (40 mL, 4.3 mmol). The reaction mixture was stirred for 24 h at room temperature, and then the solvent was removed in vacuum. The residue was extracted with hot toluene to remove the LiCl by centrifugation led to a yellow solution. Removing the toluene solvent, washing the residues with hexane, and crystallization from a mixture of THF/hexane at 0 °C gave the product **1** as yellow crystals (2.7 g, 79%). C<sub>31</sub>H<sub>68</sub>ClN<sub>6</sub>SmO<sub>2</sub>Si<sub>2</sub> (798.89) calcd.: C, 46.61;

Table 5
---------

Bond distances(Å)			
Sm(1)-O(2)	2.482 (4)	N(3)-C(2)	1.433 (8)
Sm(1)-O(1A)	2.366 (4)	N(4)-C(2)	1.392 (8)
Sm(1)-O(2A)	2.387 (4)	N(6)-C(2)	1.279 (8)
Sm(1) - N(1)	2.418 (5)	O(1)-Sm(1A)	2.366 (4)
Sm(1)-N(2)	2.415 (5)	O(2)-Sm(1A)	2.387 (4)
Sm(1)–N(7A)	2.485 (6)	N(1)-C(1)	1.322 (8)
Sm(1)–N(8)	2.541 (5)	O(1)-C(24)	1.295 (7)
Sm(1)-C(24A)	2.834 (6)	N(7)-C(24)	1.319 (8)
Sm(1)-C(1)	2.864 (6)	N(8)-C(31)	1.289 (9)
Sm(1)-C(31)	2.942 (7)	O(2)-C(31)	1.317 (7)
Bond angles (°)			
O(1A)-Sm(1)-O(2A)	82.25 (15)	O(1A) - Sm(1) - O(2)	115.89 (15)
O(1A) - Sm(1) - N(2)	135.51 (18)	O(2A)-Sm(1)-O(2)	66.82 (16)
O(2A) - Sm(1) - N(2)	88.52 (17)	N(2)-Sm(1)-O(2)	99.61 (17)
N(2)-Sm(1)-N(1)	55.00 (18)	O(2A) - Sm(1) - N(7A)	125.35 (16)
N(2)-Sm(1)-N(7A)	145.25 (18)	N(1)-Sm(1)-N(7A)	93.64 (18)
N(1)-C(1)-N(2)	114.3 (6)	C(2) - N(4) - C(5)	120.4 (5)
N(4)-C(2)-N(3)	116.1 (6)	N(6)-C(2)-N(3)	126.8 (6)



Scheme 6. The possible mechanism for the formation of complex 6.

H, 8.58; N, 10.52; Sm, 18.82. Found: 46.92; H, 8.73; N, 10.19; Sm, 18.47. IR (KBr, cm<sup>-1</sup>): 2971 (s), 2875 (m), 1620 (s), 1520 (m), 1469 (m), 1216 (m), 1164 (m), 891 (w), 841 (m), 624 (w).

#### 3.4. Synthesis of LSmCl(DME) (2)

Complex **1** (1.28 g, 1.6 mmol) was dissolved in DME (15 mL). Removing the DME solvent, washing the residues with hexane, and crystallization from a mixture of THF and hexane at 0 °C gave the product **2** as yellow crystals (0.95 g, 80%).  $C_{27}H_{62}ClN_6O_2Si_2Sm$  (744.80) calcd.: C, 43.54; H, 8.39; N, 11.28; Sm, 20.19. Found: C, 43.09; H, 8.18; N, 11.51; Sm, 20.57. IR (KBr, cm<sup>-1</sup>): 2974 (s), 2871 (m), 1618 (s), 1385 (m), 1164 (m), 605 (m).

# 3.5. Synthesis of $LSm(\eta^1-CH_2C_6H_5)(DME)$ (3)

To a THF solution (20 mL) of **1** (2.0 g, 2.5 mmol) was added  $KCH_2C_6H_5$  (0.325 g, 2.5 mmol) at 0 °C. The mixture was allowed to slowly warm to room temperature and stirred for 12 h. The KCl precipitation was removed by centrifugation led to a yellow solution. Removing the THF solvent, washing the residues with hexane, and crystallization from a mixture of DME and hexane at 0 °C gave the product **3** as yellow crystals (1.16 g, 58%).  $C_{34}H_{69}N_6O_2Si_2Sm$  (800.48) calcd: C, 51.01; H, 8.69; N, 10.50; Sm, 18.78. Found: C, 50.34; H, 8.41; N, 10.77; Sm, 19.12. IR (KBr, cm<sup>-1</sup>): 2965 (s), 1628 (s), 1468 (s), 1368 (m), 1160 (m), 842 (m).

### 3.6. Reaction of 3 with CH<sub>3</sub>CN to afford complex 4

To a toluene solution (20 mL) of  $\mathbf{3}$  (0.96 g, 1.2 mmol) was added acetonitrile (2.4 mL, 1 M in THF). The resulting solution was stirred overnight at room temperature. After the clear solution was

concentrated, pale yellow crystals of **4** (0.59 g, yield 64%) were isolated at 0 °C.  $C_{62}H_{130}N_{16}O_2Si_4Sm_2$  (1544.86) calcd.: C, 48.20; H, 8.48; N, 14.51; Sm, 19.47. found: C, 48.68; H, 8.31; N, 14.77; Sm, 19.22. IR (KBr, cm<sup>-1</sup>): 3414 (s), 2972 (s), 2187(s), 1617 (s), 1524 (m), 1468 (m), 1384 (m), 1170 (w), 839 (w).

### 3.7. Reaction of **3** with 4-MeOC<sub>6</sub>H<sub>4</sub>CN to afford complex **5**

To a hexane solution (20 mL) of **3** (0.66 g, 0.82 mmol) was added 4-MeOC<sub>6</sub>H<sub>4</sub>CN (0.11 g, 0.82 mmol, dissolved in 2 mL THF). The resulting solution was stirred overnight at room temperature. After the clear solution was concentrated, pale yellow crystals of **5** (0.41 g, yield 59%) were isolated at 0 °C.  $C_{76}H_{132}N_{14}O_2Si_4Sm_2$  (1687.01) calcd.: C, 54.11; H, 7.89; N, 11.62; Sm, 17.83. found: C, 54.68; H, 8.03; N, 11.36; Sm, 18.19. IR (KBr, cm<sup>-1</sup>): 3415 (s), 2970 (s), 1618 (s), 1508 (w), 1384 (s), 1171 (w), 839 (w).

# 3.8. Reaction of **3** with phenyl PhNCO to afford complex **6**

To a hexane (20 mL) solution of **3** (0.80 g, 1.0 mmol) was added PhNCO (2.0 mL, 1 M in THF). The resulting solution was stirred overnight at room temperature. After the clear solution was concentrated, pale yellow crystals of **6** (0.58 g, yield 61%) were isolated.  $C_{88}H_{138}N_{16}O_4Si_4Sm_2$  (1897.20) calcd.: C, 55.71; H, 7.33; N, 11.81; Sm, 15.85. Found: C, 56.32; H, 7.60; N, 11.45; Sm, 15.98. IR (KBr, cm<sup>-1</sup>): 2968 (s), 1620 (s), 1531 (m), 1498 (m), 1442 (m), 1384 (m), 1168 (w), 843 (w).

# 4. Conclusion

This investigation shows that bridged guanidinates ligand can be used to stabilize a variety of Sm–X (X = Cl, C, and heteroatom)

bonds in the form of complexes LSmX. The reaction of LSm( $\eta^{1}$ - $CH_2C_6H_5)(DME)$  (3) with MeCN proceeds rapidly to provide the complex via metalation of methyl group of an acetonitrile, followed by insertion reaction of the second coordinated acetonitrile into the newly formed Ln-alkyl species. This reaction is very similar to that of [Me<sub>2</sub>Si(NCMe<sub>3</sub>)(OCMe<sub>3</sub>)]<sub>2</sub>YCH(SiMe<sub>3</sub>)<sub>2</sub> [41]. However, the reaction of **3** with 4-MeOC<sub>6</sub>H<sub>4</sub>CN affords the insertion product with 1.3-H shift. A double insertion reaction with a ligand rearrangement is observed during the reaction of **3** with PhNCO. This result clearly demonstrates the limited suitability of bridged guanidinates ligand to be applied as inert spectator ligands, as the fluxionality of guanidinate group in binding fashion.

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#### **Appendix A. Supplementary material**

CCDC 875078 (1), 875079 (2), 875080 (3), 875081 (5), 875082 (4), 875083 (6) contain the supplementary crystallographic data for complexes 1–6. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/ data request/cif.

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