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Unprecedented reaction of bridged bis(guanidinate) lanthanide complexes: Sterically induced deprotonation

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Unprecedented reaction of bridged bis(guanidinate) lanthanide complexes: Sterically induced deprotonation

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Reaction of $LnCl_3$ with lithium salt of bridged bis(guanidinate) bearing a rigid naphthalene linker $[Li_2\{LH_2\}_2Li_2]$ ($LH_2 = 1,8\text{-}C_{10}H_6\{NC(N^iPr)(NH^iPr)\}_2$) (**1**), which was synthesized by the reaction of 1,8-diaminonaphthalene with 2 equiv of ^nBuLi, followed by treatment with 2 equiv of N,N'-diisopropylcarbodiimide, yielded the chlorides $[LnCl\{LH_2\}]$ (Ln = Yb (**2**), Y (**3**)) in good yields. Metathesis reaction of **2** and **3** with $NaN(SiMe_3)_2$ did not afford the corresponding amide complexes, but the deprotonation products of $[Ln\{LH\}]_2$ ($LH = 1,8\text{-}C_{10}H_6\{NC(N^iPr)(NH^iPr)\}\{NC(N^iPr)_2\}$; Ln = Yb (**4**), Y (**5**)) were isolated instead. The LH in **4** and **5** both act as a bridging ligand binding to two metals in a μ-η^1:η^2:η^2 fashion, and the re-arrangement of LH occurred during the reaction. The size of the amido group was found to have a great influence on the outcome of the metathesis reaction. Reaction of **2** with bulky $NaNH(C_6H_3{}^iPr_2\text{-}2,6)$ afforded **4** as the only product, whereas the same reaction with less bulky $LiNH(C_6H_4Cl\text{-}4)$ and $LiNH(C_6H_4CH_3\text{-}4)$ led to the corresponding amides, $[Yb\{LH_2\}(NHC_6H_4Cl\text{-}4)]_2$ (**6**) and $[Yb\{LH_2\}(NHC_6H_4CH_3\text{-}4)]_2$ (**7**), respectively. The re-arrangement of ligand was also observed in both cases. A possible pathway for the deprotonation of LH_2 was discussed. Molecular structures of **1-7** were determined by X-ray single crystal analysis.

20 **Introduction**

Monoanionic guanidinate groups, as one of the important non-cyclopentadienyl ligands, have been widely used in organolanthanide chemistry as ancillary ligands, due to their strong binding to the lanthanide metals and tunable electronic and steric factors.[1] The N,N',N''-trialkylguanidinates in these monoanionic ligand sets are of interest because they can transfer to highly reactive dianionic species under certain

conditions.[2-6] For example, the dianionic guanidinate metal complexes react facilely with Me_3SiCl to yield a Me_3Si- modified monoanionic guanidinate complexes,[4d,7] and the dianionic guanidinate Ti complex was found not only to react with amine leading to an imido complex *via* de-guanidine, but also as an active species for addition of amines to carbodiimides to guanidines.[8] Till now several routes to dianionic

5   guanidinate species have been explored. They are cycloaddition of transition metal imido complexes with carbodiimides,[2] the reaction of $[PtCl_2(cod)]$ with *N,N',N''*-triphenylguanidine,[3] and the deprotonation reaction of a coordinated monoanionic guanidinate using alkyl or amido metal reagents,[4] or by either guanidine elimination,[5] or amine elimination.[6] Here we report the first example of sterically induced deprotonation of a coordinated bridged bis(guanidinate) ligand in lanthanide complexes, which leads to

10   the formation of bridged (mono- and dianionic)guanidinate lanthanide complexes, and their reactivity towards aromatic amines NH_2Ar (Ar = C_6H_4Cl-4 and $C_6H_4CH_3$-4) to binuclear bridged bis(monoanionic guanidinate) lanthanide amides. The syntheses of the lithium salt of a novel naphthalene bridged bis(guanidinate) ligand and the corresponding lanthanide chlorides, as well as the metathesis reaction of the chlorides with alkali metal salts of amines are also described.

15   **Results and discussion**

Synthesis and characterization of $[Li_2\{LH_2\}_2Li_2]$ (LH_2 = 1,8-$C_{10}H_6\{NC(N^iPr)(NH^iPr)\}_2$) (1)

Our recent work shows that the bridged bis(guanidinate) with a soft linker was shown to be suitable coordination platform, which allows the synthesis of isolable lanthanide monoborohydride and benzyl complexes.[9] Thus, a novel bridged bis(guanidinate) ligand precursor with a rigid naphthalene linker, LH_4

20   (LH_4 = 1,8-$C_{10}H_6\{NC(NH^iPr)_2\}_2$), was designed and the lithium salt $[Li_2\{LH_2\}_2Li_2]$ (**1**) was synthesized in 83% yield by the reaction of 1,8-diaminonaphthalene with 2 equiv of ^nBuLi, followed by treatment with 2 equiv of *N,N'*-diisopropylcarbodiimide in a THF solution (Scheme 1).

Complex **1** was fully characterized by NMR spectroscopy, elemental analysis as well as X-ray crystal structure analysis.
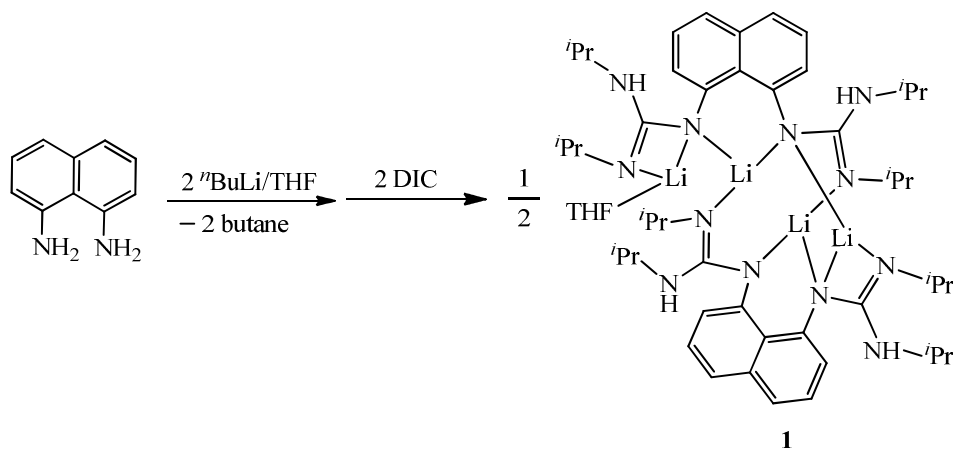
Scheme 1 Synthesis of **1**.

The molecular structure of **1** with the selective bond lengths and angles is shown in Fig. 1. **1** is a tetrametallic complex consisting of four Li atoms, two LH_2 groups and one THF molecule. Each Li atom is three-coordinate. The coordinated environment around the Li atoms can be divided into three types: Li(1) is ligated by two nitrogen atoms (N(1) and N(2)) of one guanidinate group from one LH_2 and one nitrogen atom (N(7)) from the second LH_2; Li(2) and Li(3) both are around by two nitrogen atoms attached to the bridge from one LH_2 and the third nitrogen atom at the ^{i}Pr group of the second LH_2, while Li(4) is coordinated by two nitrogen atoms (N(10) and N(11)) of one guanidinate from one LH_2 and one oxygen atom from the THF molecule.

The three C-N bond lengths of each guanidine group (C(2)-N(4) 1.381(5) Å, C(2)-N(5) 1.310(5) Å and C(2)-N(6) 1.395(5) Å) indicate that the π electron of the C=N double bond is not delocalized within the CN_3 unit. The same bonding type is also found in the complexes with the severe steric bulky amidinate or guanidinate ligands.[10] The N-Li-N bond angles vary from 66.3° for the chelating guanidinates to 136.1° for the bridging ones. The Li-N bond distances span a range from 1.919(9) to 2.234(9) Å. Thus the structure is similar to those of other known Li guanidinates.[11]

Synthesis and characterization of [LnCl{LH$_2$}] (Ln = Yb (2), Y (3))

Reaction of anhydrous $LnCl_3$ with 0.5 equiv of **1** in THF at room temperature for 24 h afforded the monochlorides [LnCl{LH$_2$}] (Ln = Yb (**2**), Y (**3**)) in the yields of 70% for **2** and 66% for **3** (Scheme 2).

Complexes **2** and **3** were obtained as air and moisture sensitive crystalline solids upon crystallization from

a mixture of THF/hexane. They are soluble in THF and toluene and poorly soluble in hexane.

Elemental analysis is consistent with their formulae. The ^{1}H NMR spectra of the diamagnetic **3** in

C_6D_6 show the expected sets of signals assigned to the LH_2 and the coordinated THF molecule.

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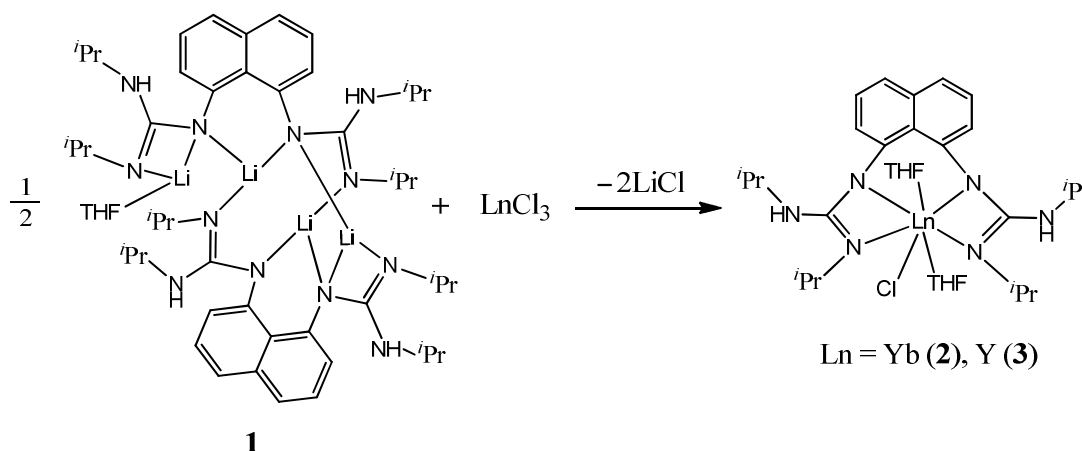
Scheme 2 Synthesis of complexes **2** and **3.**

Complexes **2** and **3** were further confirmed by X-ray single-crystal structure analysis. The molecular

structures of **2** and **3** are shown in Fig. 2 as they are isostructural. Selected bond lengths and angles are

listed in Table 1.

10   Both complexes crystallize in the monoclinic space group C2/c with the Yb(Y) atom, the Cl atom and

the two carbon atoms of the linker, C(6) and C(7), lying on a crystallographic two fold axis (thus, only half

the molecule is unique). Each metal atom is bound by two guanidinate groups in a η^2-fashion with one

chlorine atom and two THF molecules completing each coordination sphere. The center metal in each

complex is five-coordinate, and adopts a pseudo-trigonal-bipyramidal geometry, if the guanidinate groups

15   are considered to be point donors located at the central carbon atoms. The dihedral angle of the two Ln-N-

C-N planes here is 0.83° for **2** and 2.26° for **3**, which is consistent with those found in the analogues

reported.[12] The Yb-Cl (Y-Cl) distance (Table 1) is comparable with those in the related complexes [(e.g.,

five-coordinate bridged bis(amidinate) Yb(Y) chloride,[13] average 2.634 Å and five-coordinate bridged

bis(guanidinate) Yb(Y) chloride,[9a] average 2.640 Å). The π electron of the C=N double bond is not

delocalized within the CN_3 unit as confirmed by the bond distances of C=N (Table 1). The bond distances of metal to the guanidinate group are comparable with those reported for the related complexes.[14]

Reactions of 2 (or 3) with alkali metal amides: Sterically induced deprotonation to bridged (mono- and dianionic)guanidinate lanthanide complexes, [Ln{LH}]$_2$ (LH = 1,8-C$_{10}$H$_6${NC(N^{i}Pr)(NH^{i}Pr)}{NC(N^{i}Pr)$_2$}; Ln = Yb (4), Y (5)), and the influence of amido group

Reactions of 2 and 3 with NaN(SiMe$_3$)$_2$ to 4 and 5

It is unexpected that the reaction between NaN(SiMe$_3$)$_2$ and **2** in THF at a molar ratio of 1:1 did not give the amide complex [Yb{LH$_2$}N(SiMe$_3$)$_2$], but the complex [Yb{LH}]$_2$ (**4**) with bridged (mono- and dianionic)guanidinate ligand LH was obtained in good yield *via* the deprotonation of one of the guanidinate group (Scheme 3). The formation of **4** was confirmed by elemental analysis and crystal structure determination.

The same reaction of **3** with NaN(SiMe$_3$)$_2$ afforded the analogue **5** as the only product in 60% yield (Scheme 3). Complex **5** was fully characterized by elemental analysis, ^{1}H NMR and single crystal structure determination.
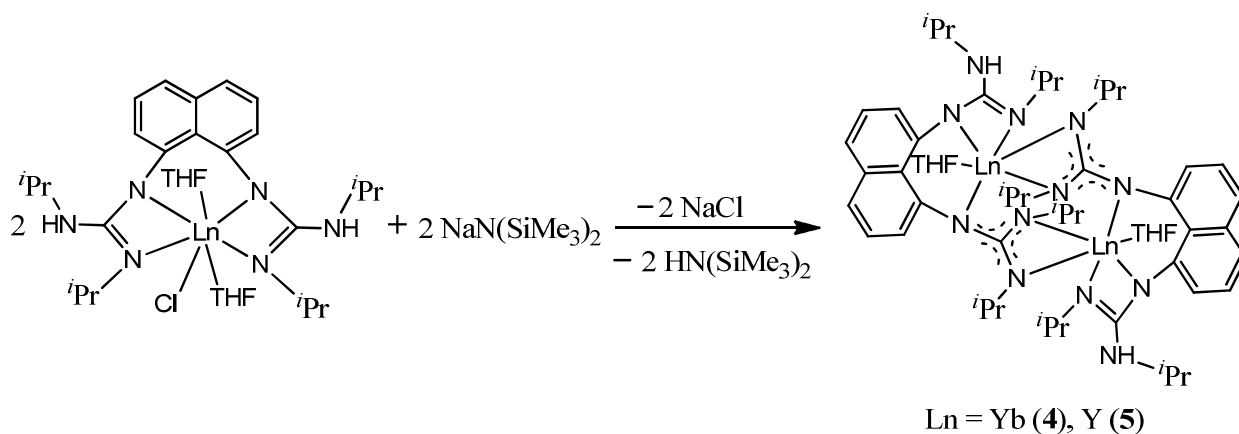
Scheme 3 Reaction of [LnCl{LH$_2$}] with NaN(SiMe$_3$)$_2$.

Complexes **4** and **5** are isostructural, their molecular structures are shown in Fig. 3. The selected bond distances and angles are given in Table 2. Both complexes crystallize in the monoclinic space group C2/c with a crystallographic inversion center located at the midpoint of Ln⋯Ln. Both have a cyclic structure

consisting of two metals, two LH and two THF molecules. The ligand LH coordinates to two metals in a μ-η^1:η^2:η^2 fashion as a bridging ligand. Thus, the re-arrangement of the ligand, which leads to the transformation of coordination mode from a chelating fashion to a bridging one, occurred during the reaction process. This may be attributed to the requirement for stabilizing **4** and **5**. Each center metal is

5   six-coordinate and bound to five nitrogen atoms of the one monoanionic guanidinate and two dianionic guanidinate groups from the two LH and one oxygen atom from the THF molecule. The coordination geometry can be described as a distorted trigonal pyramidal (assuming the guanidinate to occupy a single coordination site at the central C atom of the NCN fragment).

     The C-N bond distances of each dianionic guanidinate group (Table 2) are approximately equivalent,

10   indicating that the π electrons of the C=N double bond are delocalized over the CN_3 unit.[4d-4g,15] Whilst, the π electron of the C=N double bond in monoanionic guanidinate species is not delocalized within the CN_3 unit.

     The average bond distance of Yb-N for the monoanionic guanidiante group (2.328(7) Å) is compared to those of Yb-N in the dianionic guanidinate groups (2.322(4) Å), this may be because both dianionic

15   guanidinate groups are bridging species and the bond distances of the Yb-bridged dianionic guanidinate groups are normally longer than those of the Yb-unbridged one. The distance of Yb(Y)-O bond is normal.

Influence of the size of amido group

*Reactions of **2** with LiNH(C_6H_4Cl-4) and LiNH($C_6H_4CH_3$-4): Synthesis and characterization of*

*[Yb(NHC_6H_4Cl-4){LH$_2$}]$_2$ (**6**) and [Yb(NH$C_6H_4CH_3$-4){LH$_2$}]$_2$ (**7**)*

20   To understand the driving force for the occurrence of the deprotonation of LH$_2$, the reactions of **2** with metal salts of amide with various sizes were further investigated. The reaction of **2** with lithium salt of a less bulky aromatic amide LiNH(C_6H_4Cl-4) was first conducted. Treatment of a solution of **2** in THF with equivalent of LiNH(C_6H_4Cl-4) in THF gave a yellow solution. After workup, yellow crystals of **6** were isolated in 58% yield (Scheme 4). Elemental analysis of the crystals is in good agreement with the

25   formula. The identity of **6** was unequivocally established by an X-ray structure determination.

Replacing $LiNH(C_6H_4Cl-4)$ by almost the same size lithium amide, $LiNH(C_6H_4CH_3-4)$, also led to the formation of the analogous amide complex **7** as yellow crystals in 62% yield (Scheme 4). Complex **7** was confirmed by single-crystal structure analysis. Complexes **6** and **7** are extremely air and moisture sensitive. They are soluble in THF and sparingly soluble in hexane.

$Ar = 4\text{-}ClC_6H_4$ (**6**), $4\text{-}CH_3C_6H_4$ (**7**)
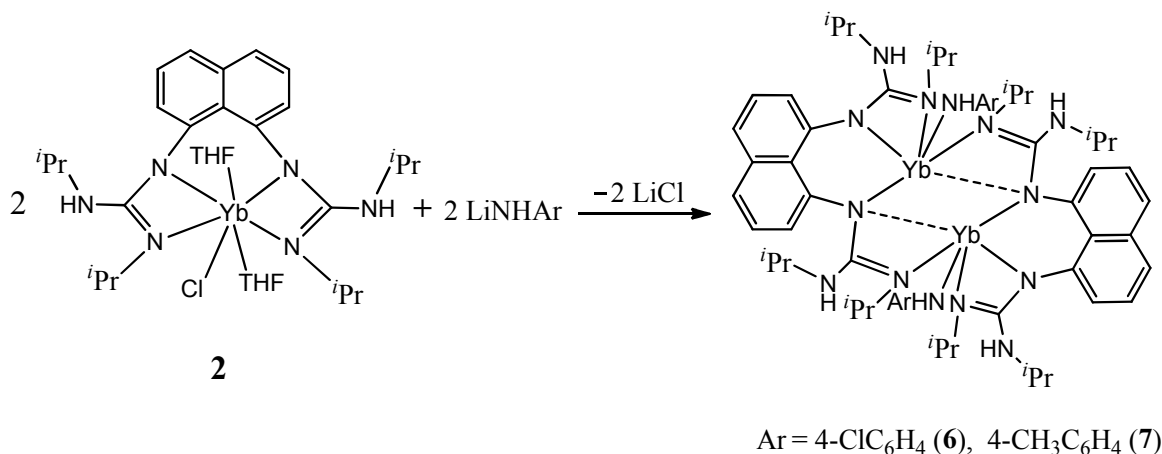
**Scheme 4** Preparations of **6** and **7.**

The molecular structures of **6** and **7** are depicted in Fig. 4 and 5, respectively. Selected bond distances and angles are listed in Table 3. Complexes **6** and **7** both crystallize in the triclinic space group P$\bar{1}$ with a crystallographic inversion center located at the center of the Yb_2N_2 (Yb(1), Yb(1A), N(1) and N(1A)) core. Both are binuclear cyclic complexes in which the two Yb-N(amide) moieties are connected together by the two LH_2 groups. Both LH_2 ligands adopt a $\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$ coordination fashion. Obviously, the re-arrangement of the ligand from a chelating to a bridging one occurred during the metathesis reaction. The re-arrangement of a bridged LH_2 ligand here, similar to the case mentioned above, might be attributed to the overcrowded coordination environment around the central metal in the original state.[16] Each center metal in both complexes is six-coordinate and bound to five nitrogen atoms of the three guanidinate fragments from the two LH_2 ligands and one amido group. The coordination geometry is a pseudo-trigonal pyramidal (assuming the guanidinate to occupy a single coordination site at the central C atom of the CN_3 fragment).

The average bond distances of Yb-N(guanidinate) fall in the ranges of lanthanide guanidinate complexes.[1,9] The π electron of the C=N double bond is not delocalized within the CN_3 unit, which is as

same as those in **2**, **3** and the other related complexes.[4c,10c] The distance of Yb-N(amide) (2.206(5) Å for **6**

and 2.181(5) Å for **7**) is comparable with those found in lanthanide amide complexes reported

previously.[17]

*Reaction of 2 with LiNH($C_6H_3{}^iPr_2$-2,6): Formation of 4*

5   However, the further reaction of **2** with the bulky sodium salt of amide NaNH($C_6H_3{}^iPr_2$-2,6) resulted in the

occurrence of deprotonation reaction of LH$_2$, affording **4** as the only product in 56% yield, and no amide

complex [Yb(NHC$_6$H$_3{}^i$Pr$_2$-2,6){LH$_2$}]$_2$ could be obtained (Scheme 5). These results demonstrated that the

metathesis reaction of **2** with metal amide is very sensitive to the size of the amido group.
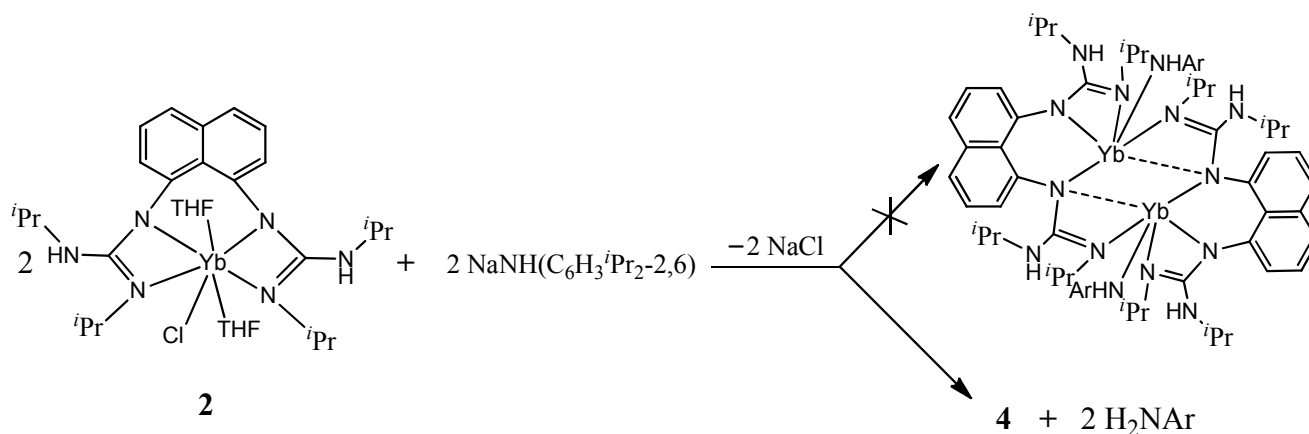
10   **Scheme 5**   Reaction of **2** with NaNH($C_6H_3{}^iPr_2$-2,6)**.**

Possible mechanism for the formation of 4 and 5

Based on the above results, we may propose that the overcrowded coordination environment in lanthanide

amide formed, rather than the nucleophilic attack of MNHAr to LH$_2$, leads to the further deprotonation of

LH$_2$, although the detailed mechanism for the double deprotonation of LH$_4$ has not been clear. Thus, the

15   pathway for the deprotonation via amine-elimination is proposed as shown in Scheme 6.
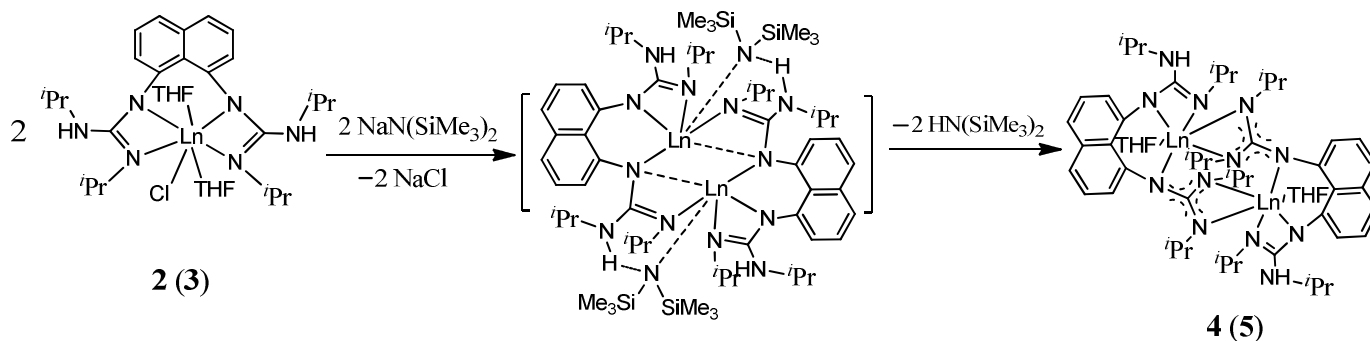
Scheme 6 Possible pathway for the formation of **4** and **5**.

The reaction of $[LnCl\{LH_2\}]$ with $NaN(SiMe_3)_2$ affords an unstable transient $[\{Ln\cdots N(SiMe_3)_2\}\{LH_2\}]_2$ with a loose $-N(SiMe_3)_2$ farther from the Ln ion than their usual optimal distance. The loose $-N(SiMe_3)_2$ group in the transient is not electro-statically stabilized as effectively as it is in conventional amide complexes, such as **6** and **7**. Thus, the unstable $[\{Ln\cdots N(SiMe_3)_2\}\{LH_2\}]_2$ transfers to the stable complex **4** (or **5**) via elimination of $HN(SiMe_3)_2$.

Reactivity of 4 toward NH$_2$Ar (Ar = C$_6$H$_4$Cl-4 and C$_6$H$_4$CH$_3$-4): A facile route for the preparation of 6 and 7

The reactivity of bianionic guanidinate Ti complex $[Ti\{(Me_2N)C(N^iPr)_2\}_2\{^iPrNC(NC_6F_5)(N^iPr)\}]$ toward amine was reported to yield an imido complex with the formation of guanidine.[8] Thus, the reactivity of **4** towards NH$_2$Ar was investigated.

Treatment of **4** with 2 equiv of $NH_2(C_6H_4Cl-4)$ in THF at room temperature led to the color change of the solution from red to yellow immediately. Removing the volatiles, washing with hexane, and extracting with toluene gave yellow crystals in 51% yield upon crystallization. The crystals were confirmed by determination of the unit cell of the single crystals to be **6**. Also the same reaction with $NH_2(C_6H_4CH_3-4)$ afforded the yellow crystals, which were characterized to be **7** as shown in Scheme 7. The reaction was not effected by either electron-withdrawing substituent (-Cl) or electron-donating substituent (-CH$_3$) at the phenyl ring of aromatic amines. However, the reaction is sensitive to the size of the amine.

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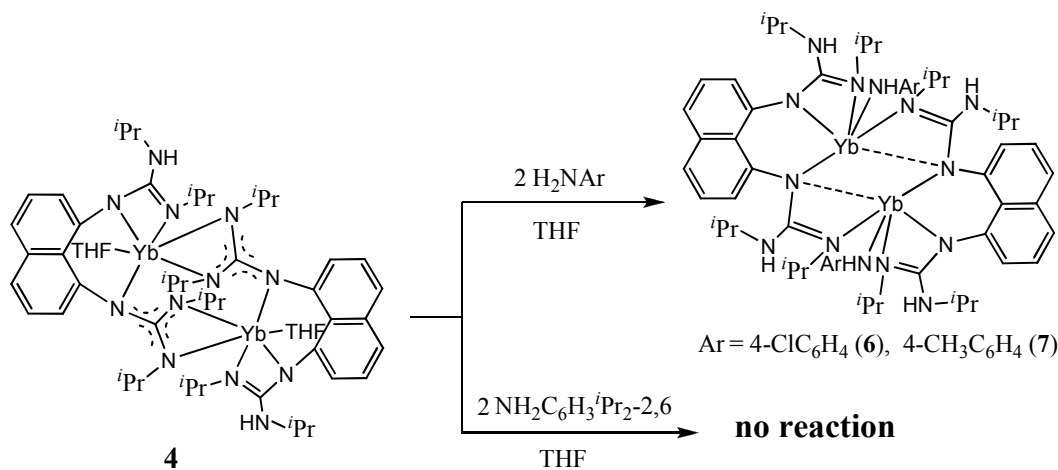
Scheme 7 Reactivity of **4** toward aromatic amines**.**

When **4** was treated with bulkier amine, $NH_2(C_6H_3{}^iPr_2\text{-}2,6)$, no reaction was observed (Scheme 7). The failure in the formation of $[Yb(NHC_6H_3{}^iPr_2\text{-}2,6)\{LH_2\}]_2$, which is in accordance with the result

5   obtained from the metathesis of **2** with $LiNH(C_6H_3{}^iPr_2\text{-}2,6)$ (see above paragraph), is not surprised and might be attributed to the instability of the overcrowded $[Yb(NHC_6H_3{}^iPr_2\text{-}2,6)\{LH_2\}]_2$ formed in *situ*.

Reaction of **4** with $[HNEt_3][BPh_4]$ was tried in an attempt to synthesize a corresponding cationic guanidinate complex. However, the reaction did not occur and the starting materials were recovered.

Conclusion

10   The new tetranuclear lithium salt of bridged bis(guanidinate) with a rigid naphthalene linker $[Li_2\{LH_2\}_2Li_2]$ and the lanthanide chlorides $[LnCl\{LH_2\}]$ were prepared. The deprotonation of the LH_2 in a highly encumbered lanthanide amide complex has been explored. To our best knowledge, this is the first example of sterically induced deprotonation of a coordinated bridged bis(guanidinate) ligand in lanthanide complexes. Thus, the size of the amido group is found to have a great influence on the outcome of the

15   metathesis reaction between $[LnCl\{LH_2\}]$ and alkali metal amides: corresponding amide complexes **6** and **7** could be prepared using less bulky metal amides, whereas the deprotonation products **4** and **5** were isolated by use of bulky metal amides. Reaction of **4** with appropriate aromatic amines afforded lanthanide amide complexes, which represents an alternative route for the synthesis of lanthanide amides. The high

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reactivity of [Yb{LH}]$_2$ is likely to find more general applications in synthesis of metal complex. The related work is ongoing.

Experimental

General procedures

5   All manipulations and reactions described below were carried out under a purified argon atmosphere using standard Schlenk or glovebox techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon before use. N,N'-diisopropylcarbodiimide was purchased from Alfa Aesar and dried over CaH$_2$ for 48 h and distilled under reduced pressure. The other reagents were purchased from Acros Chemical and used as received without further purification. The ^{1}H and ^{13}C NMR spectra were

10   recorded in a C$_6$D$_6$ solution for complexes **1**, **3** and **5** with a Unity Varian spectrometer. Because of their paramagnetism, no resolvable NMR spectrum for the other complexes was obtained. Elemental analysis was performed by direct combustion using a Carlo-Erba EA 1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets.

[Li$_4$\{LH$_2$\}$_2$(THF)] (1). To a solution of 1,8-Diaminonaphthalene (1.45 g, 9.16 mmol) in THF (30

15   mL) was slowly added a solution of ^{n}BuLi in hexane (6.59 mL 2.78 M, 18.32 mmol) at 0 ^{o}C. The reaction mixture was stirred for 6 h. N,N'-diisopropylcarbodiimide (2.86 mL, 18.32 mmol) was then added dropwise to the solution. The mixture was stirred for 24 h, after which the solvent was removed to dry under vacuum conditions. The product was extracted with a mixture of THF/hexane. Cooling to 0 ^{o}C yielded colorless crystals of **1** (3.49 g, 83%). Anal. Calcd for C$_{52}$H$_{80}$N$_{12}$OLi$_4$ (917.04): C, 68.10; H, 8.72;

20   N, 18.32%. Found: C, 67.99; H, 8.69; N, 18.41%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.37-6.38 (m, 12H, Ar-H), 4.15-2.83 (m, 16H, NH, α-CH$_2$ THF and CH(CH$_3$)$_2$), 1.43-1.30 (m, 4H, β-CH$_2$ THF), 1.28-0.40 (m, 48H, CH$_3$). ^{13}C NMR (75 MHz, C$_6$D$_6$): 163.8 (C=N), 162.4 (C=N), 162.3 (C=N), 161.9 (C=N), 156.5 (Ar), 153.6 (Ar), 151.5 (Ar), 149.1 (Ar), 140.7 (Ar), 139.3 (Ar), 138.9 (Ar), 126.7 (Ar), 126.4 (Ar), 125.7 (Ar), 125.0 (Ar), 124.6 (Ar), 121.6 (Ar), 119.1 (Ar), 117.4 (Ar), 115.8 (Ar), 114.9 (Ar), 113.8 (Ar), 113.1

(Ar), 107.9 (Ar), 67.7 (α-CH$_2$ THF)，46.9 (CH(CH$_3$)$_2$), 46.2 (CH(CH$_3$)$_2$), 45.9 (CH(CH$_3$)$_2$), 45.8 (CH(CH$_3$)$_2$), 45.2 (CH(CH$_3$)$_2$), 44.5 (CH(CH$_3$)$_2$), 43.9 (CH(CH$_3$)$_2$), 43.5 (CH(CH$_3$)$_2$), 27.0 (CH$_3$), 26.1 (CH$_3$), 25.8 (CH$_3$), 25.7 (CH$_3$), 25.6 (CH$_3$), 25.3 (β-CH$_2$ THF), 24.8 (CH$_3$), 24.6 (CH$_3$), 24.5 (CH$_3$), 24.1 (CH$_3$), 23.7 (CH$_3$), 23.5 (CH$_3$), 23.2 (CH$_3$). IR (KBr, cm^{-1}): 3270 (m), 2963 (s), 1630 (s), 1573 (s), 1493 (s), 1465 (s), 1384 (m), 1230 (s), 1157 (s), 863 (m), 763 (w), 624 (w), 505 (m).

[YbCl{LH$_2$}(THF)$_2$] (2). A white suspension of YbCl$_3$ (2.45 g, 8.78 mmol) in THF (20 mL) was added to a solution of **1** (4.02 g, 4.39 mmol) in THF (20 mL). The mixture was stirred for 24 h at room temperature, and then the solvent was removed to dry under vacuum conditions. The residue was extracted with toluene and the LiCl was removed by centrifugation. The extracts were concentrated and cooled to 0 ^{o}C. Complex **2** was obtained as yellow crystals in a few days (4.68 g, 70%). Anal. Calcd for C$_{32}$H$_{52}$ClN$_6$O$_2$Yb (761.29): C, 50.48; H, 6.83; N, 11.03%. Found: C, 50.11; H, 6.67; N, 10.90%. IR (KBr, cm^{-1}): 3270 (w), 2972 (m), 2870 (w), 1614 (s), 1576 (s), 1384 (m), 1241 (m), 1158 (s), 864 (w), 765 (m), 504 (m).

[YCl{LH$_2$}(THF)$_2$] (3). The synthesis of complex **3** was carried out in the same way as that described for complex **2**. Pale yellow crystals were obtained at 0 ^{o}C (3.92 g, 66%). Anal. Calcd for C$_{32}$H$_{52}$ClN$_6$O$_2$Y (677.16): C, 56.75; H, 7.68; N, 12.40%. Found: C 56.31; H, 7.47; N, 12.64%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.50-6.35 (m, 6H, Ar-H), 4.10-3.15 (br, 14H, NH, α-CH$_2$ THF and CH(CH$_3$)$_2$), 1.81-0.40 (m, 32H, β-CH$_2$ THF and CH$_3$). ^{13}C NMR (101 MHz, C$_6$D$_6$): 164.4 (C=N), 146.3 (Ar), 138.5 (Ar), 125.9 (Ar), 125.3 (Ar), 117.4 (Ar), 111.2 (Ar), 69.7 (α-CH$_2$ THF), 46.9 (CH(CH$_3$)$_2$), 45.56 (CH(CH$_3$)$_2$), 25.7 (CH$_3$), 25.1 (β-CH$_2$ THF), 24.8 (CH$_3$), 24.6 (CH$_3$), 24.0 (CH$_3$). IR (KBr, cm^{-1}): 3273 (w), 2970 (m), 2858 (m), 1615 (s), 1588 (s), 1381 (m), 1235 (m), 1158 (s), 873 (m), 826 (w), 764 (w), 505 (m).

[Yb{LH}(THF)]$_2$ (4). *Method 1*. A solution of NaN(SiMe$_3$)$_2$ in toluene (10.0 mL, 3.00 mmol) was added to a solution of **2** (2.28 g, 3.00 mmol) in THF (20 mL) slowly under stirring at room temperature. The mixture was stirred for 24 h, and then the solvent was removed to dry under vacuum conditions. The residue was extracted with toluene and the undissolved portion was removed by centrifugation. The

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resulting red solution was concentrated at room temperature to give **4** (1.14 g, 58%) as orange crystals. Anal. Calcd for $C_{56}H_{86}N_{12}O_2Yb_2$ (1305.44): C, 51.52; H, 6.64; N, 12.88%. Found: C, 51.16; H, 6.37; N, 12.59%. IR (KBr, cm^{-1}): 3232(m), 2969 (m), 2873(w), 2186 (m), 1627 (m), 1573 (m), 1463 (w), 1384 (w), 1207 (s), 1153 (s), 821 (m), 763 (m), 636 (m) 505 (m).

5   *Method 2*. The synthesis of complex **4** was carried out in the same way as that described in method 1, but corresponding $NaNH(C_6H_3{}^iPr_2\text{-}2,6)$ (10.0 ml in toluene, 3.00 mmol) and **2** (2.28 g, 3.00 mmol) were used. The orange crystals of complex **4** were isolated (yield 1.10 g, 56%).

    [Y{LH}(THF)]₂ (5). The synthesis of complex **5** was carried out as that described for complex **4** in the method 1. Light yellow crystals of complex **5** were isolated (1.02 g, 60%). Anal. Calcd for

10 $C_{56}H_{86}N_{12}O_2Y_2$ (1137.17): C, 59.15; H, 7.62; N, 14.78%. Found: C, 58.90; H, 7.47; N, 14.54%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.40-6.70 (m, 12H, Ar-H), 4.45-3.31 (m, 18H, NH, α-CH₂ THF and CH(CH₃)₂), 1.85-0.75 (m, 56H, β-CH₂ THF and CH₃). ^{13}C NMR (101 MHz, C_6D_6): 162.1 (CN₃), 159.2 (C=N), 150.6 (Ar), 149.7 (Ar), 140.5 (Ar), 125.7 (Ar), 124.7 (Ar), 122.3 (Ar), 114.9 (Ar), 114.2 (Ar), 109.7 (Ar), 109.2 (Ar), 69.1 (α-CH₂ THF), 46.4 (CH(CH₃)₂), 45.9 (CH(CH₃)₂), 45.0 (CH(CH₃)₂), 44.5 (CH(CH₃)₂), 26.3 (CH₃),

15 26.0 (CH₃), 25.7 (CH₃), 25.6 (CH₃), 24.9 (β-CH₂ THF), 24.7 (CH₃), 24.5 (CH₃), 24.0 (CH₃), 23.1 (CH₃). IR (KBr, cm^{-1}): 3230(m), 2972(m), 2881(w), 2184 (m), 1627 (m), 1573 (m), 1462 (w), 1381 (w), 1201 (s), 1156 (s), 820 (m), 773 (s), 632 (m), 503 (m).

    [Yb(NHC₆H₄Cl-4){LH₂}]₂ (6). *Method 1*. The synthesis of complex **6** was carried out as that described for complex **4** in the method 1, but corresponding $LiNH(C_6H_4Cl\text{-}4)$ (0.40 g, 3.00 mmol) and **2**

20 (2.28 g, 3.00 mmol) were used. The yellow crystals of complex **6** were isolated (yield 1.23 g, 58%). Anal. Calcd for $C_{60}H_{82}Cl_2N_{14}Yb_2$ (1416.37): C, 50.88; H, 5.84; N, 13.84%. Found: C, 51.04; H, 5.54; N, 13.70%. IR (KBr, cm^{-1}): 3350 (s), 3297 (w), 2969 (m), 1631 (s), 1569 (s), 1500 (m), 1465 (m), 1384 (m), 1234 (s), 1157 (s), 825 (w), 700 (s), 643 (m), 555 (m).

    Method 2. A solution of $NH_2(C_6H_4Cl\text{-}4)$ (0.42 g, 3.32 mmol) in THF (10 mL) was added into a

25 solution of the complex **4** (2.17 g, 1.66 mmol) in THF (20 mL) slowly under stirring. The mixture was

stirred at room temperature for 24 h. Volatiles were removed under vacuum, and the solid residue was

crystallized from toluene at 0 °C to give 1.19 g (51%) of yellow crystals.

[Yb(NHC$_6$H$_4$CH$_3$-4){LH$_2$}]$_2$ (7). *Method 1*. The synthesis of complex **7** was carried out as that

described for complex **4** in the method 1, but corresponding LiNH(C$_6$H$_4$CH$_3$-4) (0.34 g, 3.00 mmol) and **2**

5 (2.28 g, 3.00 mmol) were used. The yellow crystals of complex **7** were isolated (yield 1.28 g, 62%). Anal.

Calcd for C$_{62}$H$_{88}$N$_{14}$Yb$_2$ (1375.54): C, 54.14; H, 6.45; N, 14.26%. Found: C, 54.46; H, 6.79; N, 14.50%.

IR (KBr, cm^{-1}): 3348 (s), 3290 (w), 2953 (m), 1630 (s), 1572 (m), 1500 (m), 1464 (m), 1384 (m), 1340

(m), 1246 (s), 1157 (s), 820 (m), 763 (w), 625 (m), 555 (m).

Method 2. The synthesis of complex **7** was carried out as that described for complex **6** in the method

10 2, but corresponding NH$_2$(C$_6$H$_4$CH$_3$-4) (0.38 g, 3.54 mmol) and **4** (2.31 g, 1.77 mmol) were used. The

yellow crystals of complex **7** were isolated (yield 1.28 g, 53%).

X-Ray crystallographic structure determinations

Crystals of complexes **1-7** suitable for X-ray diffraction were sealed in a thin-walled glass capillary filled

under argon. Diffraction data were collected on a Agilent Xcalibur CCD area detector in the ω scan mode

15 using Mo Kα radiation (λ = 0.71070 Å) for complexes **2**, **5** and **7** and on a Rigaku Saturn CCD area

detector in the ω scan mode using Mo Kα radiation (λ = 0.71075 Å) for complexes **1, 3**, **4**, and **6**. The

diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections.

Details of the intensity data collection and crystal data are given in Table 4. The structures were solved by

direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen

20 atoms were refined with anisotropic displacement coefficients. The hydrogen atoms in these complexes

were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride

on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure

factor calculations in the final stage of full-matrix least-squares refinement. The structures were solved

and refined using SHELXL-97 programs.

5 **Notes and references**

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10 (for **3**), 909532 (for **4**), 909533 (for **5**), 909534 (for **6**), 909535 (for **7**).

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Table 1 Selected bond lengths (Å) and angles (°) for complexes **2** and **3**

	2	**3**		**2**	**3**
Bond Lengths			Bond Angles		
Ln(1)-N(1)	2.284(3)	2.312(5)	N(1)-Ln(1)-N(2)	56.35(10)	56.05(15)
Ln(1)-N(2)	2.412(4)	2.432(4)	O(1)-Ln(1)-Cl(1)	91.29(6)	91.61(10)
Ln(1)-C(1)	2.780(4)	2.798(6)	C(1)-Ln(1)-Cl(1)	115.13(8)	115.8(7)
Ln(1)-Cl(1)	2.6120(14)	2.663(3)	C(1)-Ln(1)-C(1A)	129.75(17)	128.3(3)
Ln(1)-O(1)	2.337(3)	2.364(4)	O(1)-Ln-O(1A)	177.41(12)	176.8(2)
N(1)-C(1)	1.349(5)	1.361(7)	N(1)-C(1)-N(2)	113.1(3)	113.7(5)
N(2)-C(1)	1.313(5)	1.305(7)	N(2)-C(1)-N(3)	124.2(4)	123.7(5)
N(3)-C(1)	1.383(5)	1.386(7)	N(3)-C(1)-N(1)	122.7(4)	122.6(6)

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Table 2 Selected bond lengths (Å) and angles (º) for complexes **4** and **5**

	4	**5**		**4**	**5**
Bond Lengths			Bond Angles		
Ln(1)-N(1)	2.293(8)	2.329(3)	N(4)-Ln(1)-N(5)	57.9(3)	56.09(9)
Ln(1)-N(4)	2.281(8)	2.326(3)	N(2A)-Ln(1)-N(3A)	57.7(3)	56.69(9)
Ln(1)-N(5)	2.375(7)	2.428(3)	Ln(1A)-N(2)-Ln(1)	107.9(3)	107.11(10)
Ln(1)-N(2A)	2.241(8)	2.291(3)	N(1)-Ln(1)-O(1)	99.2(3)	98.19(10)
Ln(1)-N(3A)	2.431(6)	2.471(3)	O(1)-Ln(1)-C(1A)	121.7(3)	122.74(10)
Ln(1)-O(1)	2.341(7)	2.393(3)	O(1)-Ln(1)-C(2)	91.9(3)	91.38(10)
N(1)-C(1)	1.351(11)	1.380(4)	N(1)-C(1)-N(3)	130.5(8)	130.3(3)
N(2)-C(1)	1.376(11)	1.379(4)	N(1)-C(1)-N(2)	116.2(8)	114.3(3)
N(3)-C(1)	1.351(11)	1.329(4)	N(3)-C(1)-N(2)	111.9(7)	113.6(3)
N(4)-C(2)	1.385(12)	1.366(4)	N(5)-C(2)-N(6)	123.8(8)	123.5(3)
N(5)-C(2)	1.322(11)	1.321(4)	N(5)-C(2)-N(4)	112.9(8)	112.7(3)
N(6)-C(2)	1.384(12)	1.372(5)	N(6)-C(2)-N(4)	123.2(8)	123.7(3)

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Table 3 Selected bond lengths (Å) and angles (°) for complexes **6** and **7**

	6	**7**		**6**	**7**
Bond Lengths			Bond Angles		
Yb(1)-N(1A)	2.536(5)	2.560(4)	N(7)-Yb(1)-N(4)	116.8(2)	117.07(18)
Yb(1)-N(2A)	2.329(5)	2.333(4)	N(4)-Yb(1)-N(5)	58.53(18)	58.26(17)
Yb(1)-N(4)	2.238(5)	2.239(4)	N(2A)-Yb(1)-N(1A)	55.81(17)	55.48(15)
Yb(1)-N(5)	2.238(5)	2.357(4)	N(1)-Yb(1)-N(1A)	85.70(17)	86.40(14)
Yb(1)-N(1)	2.361(5)	2.350(5)	Yb(1)-N(1)-Yb(1A)	94.30(17)	114.3(3)
Yb(1)-N(7)	2.206(5)	2.181(5)	N(2)-C(1)-N(3)	125.4(6)	124.9(5)
N(1)-C(1)	1.403(8)	1.386(7)	N(2)-C(1)-N(1)	115.3(5)	115.3(4)
N(2)-C(1)	1.299(8)	1.319(7)	N(3)-C(1)-N(1)	119.2(6)	119.7(5)
N(3)-C(1)	1.344(8)	1.362(7)	N(5)-C(2)-N(4)	113.6(6)	112.6(5)
N(4)-C(2)	1.365(8)	1.375(7)	N(5)-C(2)-N(6)	123.7(6)	124.3(5)
N(5)-C(2)	1.317(8)	1.317(7)	N(4)-C(2)-N(6)	122.6(6)	122.9(5)
N(6)-C(2)	1.370(8)	1.374(7)			

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Table 4 Crystallographic Data for Complexes **1-7**

|	**1**	**2**	**3**	**4**·5(THF)	**5**·5(THF)	**6**·3(toluene)	**7**·(THF)
Formula	$C_{52}H_{80}N_{12}OLi_4$	$C_{32}H_{52}ClN_6O_2Yb$	$C_{32}H_{52}ClN_6O_2Y$	$C_{76}H_{126}N_{12}O_7Yb_2$	$C_{76}H_{126}N_{12}O_7Y_2$	$C_{81}H_{106}Cl_2N_{14}Yb_2$	$C_{66}H_{96}N_{14}OYb_2$
fw	917.04	761.29	677.16	1665.97	1497.71	1692.78	1447.65
T/K	223(2)	223(2)	223(2)	223(2)	220(2)	223(2)	220(2)
λ/Å	0.71075	0.71070	0.71075	0.71075	0.71070	0.71075	0.71070
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P$\bar{1}$	C2/c	C2/c	C2/c	C2/c	P$\bar{1}$	P$\bar{1}$
Crystal size/mm	0.70 × 0.30 × 0.30	0.60 × 0.40 × 0.30	0.70 × 0.60 × 0.40	0.60 × 0.40 × 0.35	0.60 × 0.50 × 0.30	0.80 × 0.50 × 0.40	0.40 × 0.18 × 0.15
a/Å	11.100(2)	13.8453(6)	13.835(5)	27.103(7)	27.2799(11)	11.4364(18)	11.5151(6)
b/Å	12.745(3)	12.2986(4)	12.374(5)	18.045(5)	18.1316(7)	12.8922(15)	12.9495(8)
c/Å	21.549(6)	20.3408(9)	20.243(8)	16.717(5)	16.7684(7)	15.651(3)	13.0112(7)
α /°	86.141(18)	90	90	90	90	72.96(2)	98.036(5)
β/°	85.522(18)	93.541(4)	93.448(10)	105.444(7)	105.244(4)	84.03(3)	92.863(4)
γ/°	64.633(12)	90	90	90	90	64.624(19)	116.207(6)
V/Å^3	2744.4(11)	3457.0(2)	3459(2)	7881(4)	8002.3(6)	1992.8(6)	1709.95(17)
Z/Å^3	2	4	4	4	4	1	1
D_{calcd}/g cm^{-3}	1.110	1.463	1.300	1.404	1.243	1.411	1.406
μ/mm^{-1}	0.067	2.819	1.799	2.417	1.5	2.45	2.768
F(000)	992	1556	1432	864	748	3448	738
θrange/°	3.21-25.50	2.95-25.49	3.05-25.49	3.02-25.50	3.19-25.50	3.05-25.50	3.19-25.50
Total no. of rflns	23279	6650	8940	32764	18163	16645	16040
No. of indep rflns	10188	3148	3201	7308	7422	7370	6363
R_{int}	0.074	0.0365	0.0787	0.0827	0.035	0.0511	0.052
GOF	1.076	1.031	0.964	1.188	1.04	1.101	1.039
R [$I > 2\sigma(I)$]	0.0995	0.0330	0.0748	0.0718	0.0492	0.0508	0.0434
wR	0.2415	0.0756	0.1845	0.1459	0.1279	0.1162	0.1046
Largest diff. peak and hole/e Å^{-3}	0.815, -0.519	1.302, -0.573	0.886, -1.569	0.919, -1.152	0.659, -0.665	1.091, -1.528	1.635, -1.485

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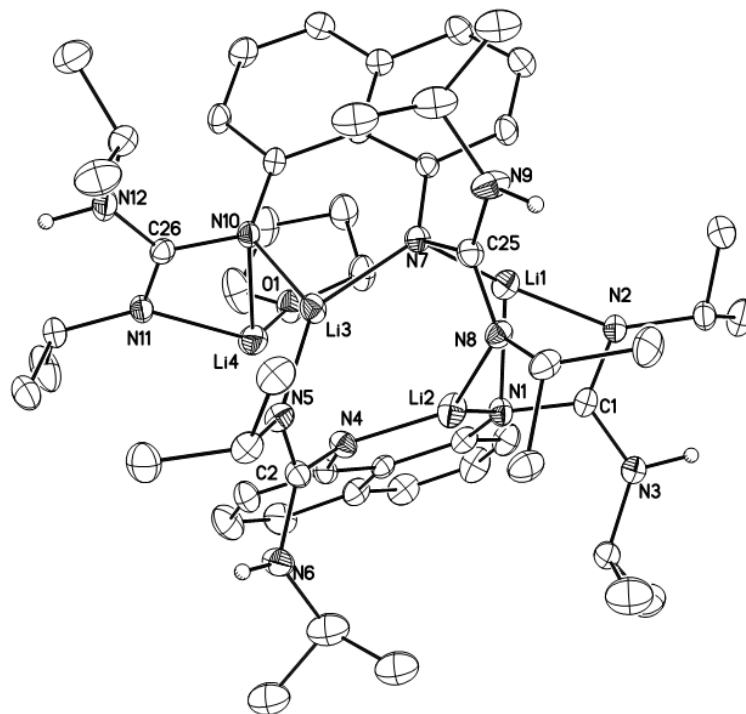
Fig. 1 Molecular structure of complex **1**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those on the nitrogen atoms) are omitted for clarity. Selected bond distances (Å) and angles (°): Li(1)-N(1) 2.147(8), Li(1)-N(2) 1.970(9), Li(1)-N(7) 2.138(9), Li(2)-N(1) 1.942(8), Li(2)-N (4) 1.919(9), Li(2)-N(8) 1.982(8), Li(3)–N(5) 2.003(7), Li(3)-N(7) 1.964(8), Li(3)-N(10) 1.933(7), Li(4)-N(10) 2.234(9), Li(4)-N(11) 1.960(9), Li(4)-O(1) 1.888(9), N(1)-C(1) 1.400(5), N(2)-C (1) 1.306(5), N(3)-C(1) 1.374(5), N(4)-C(2) 1.381(5), N(5)-C(2) 1.310(5), N(6)-C(2) 1.395(5), N(7)-C(25) 1.382(5), N(8)-C(25) 1.310(5), N(9)-C(25) 1.380(5), N(10)-C(26) 1.403(5), N(11)-C(26) 1.294(5), N(12)-C(26) 1.382(5), N(2)-Li(1)-N(1) 68.3(3), N(4)-Li(2)-N(8) 136.1(4), N(7)-Li(3)-N(5) 134.8(4), N(11)-Li(4)-N(10) 66.3(3).

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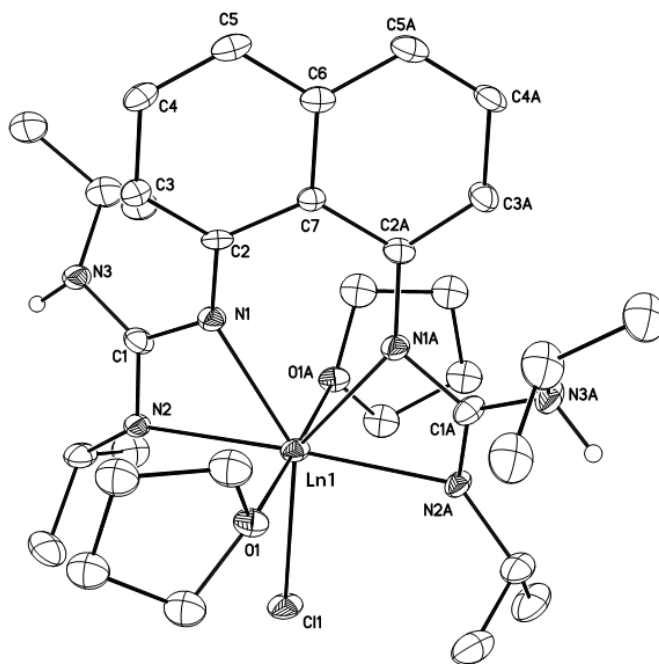
Fig. 2 Molecular structures of complexes **2** and **3**. Thermal ellipsoids are drawn at the 30% probability

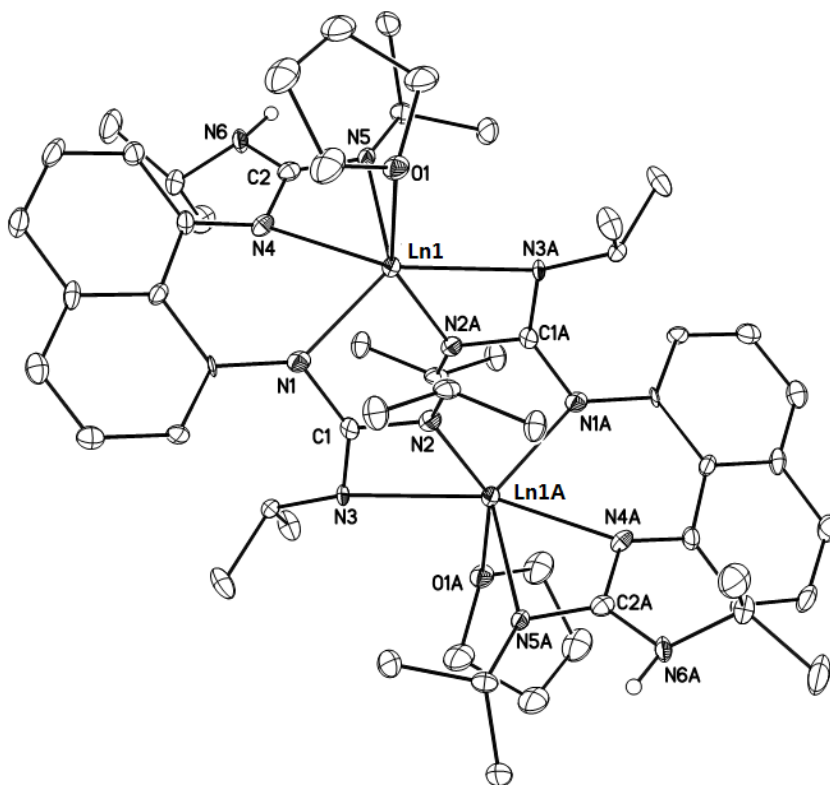level. Hydrogen atoms (except those on the nitrogen atoms) are omitted for clarity.

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Fig. 3 Molecular structures of complexes **4** and **5**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those on the nitrogen atoms) and free THF molecules in the lattice are omitted for clarity.
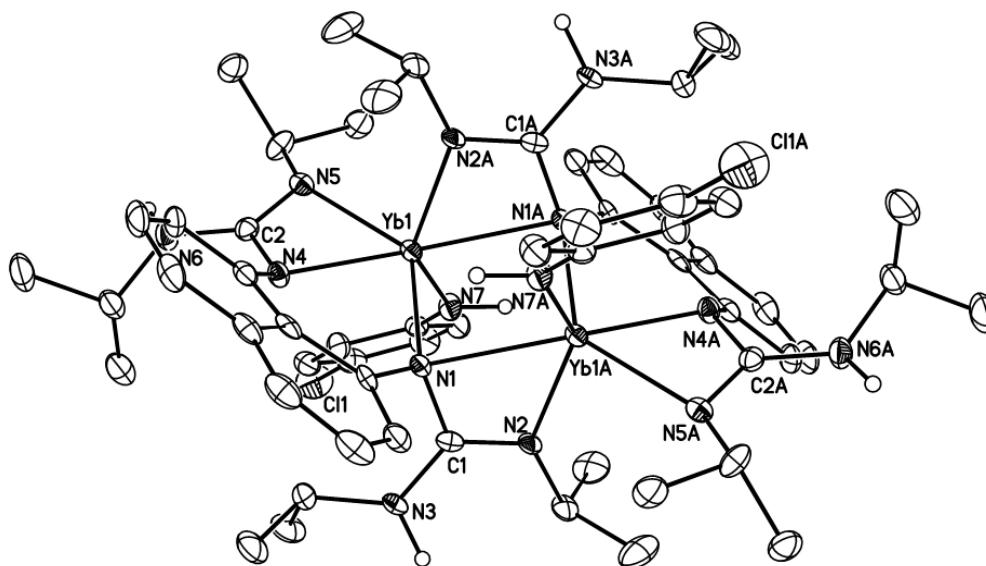
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Fig. 4 Molecular structure of complex **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those on the nitrogen atoms) and free toluene molecules in the lattice are omitted for clarity.
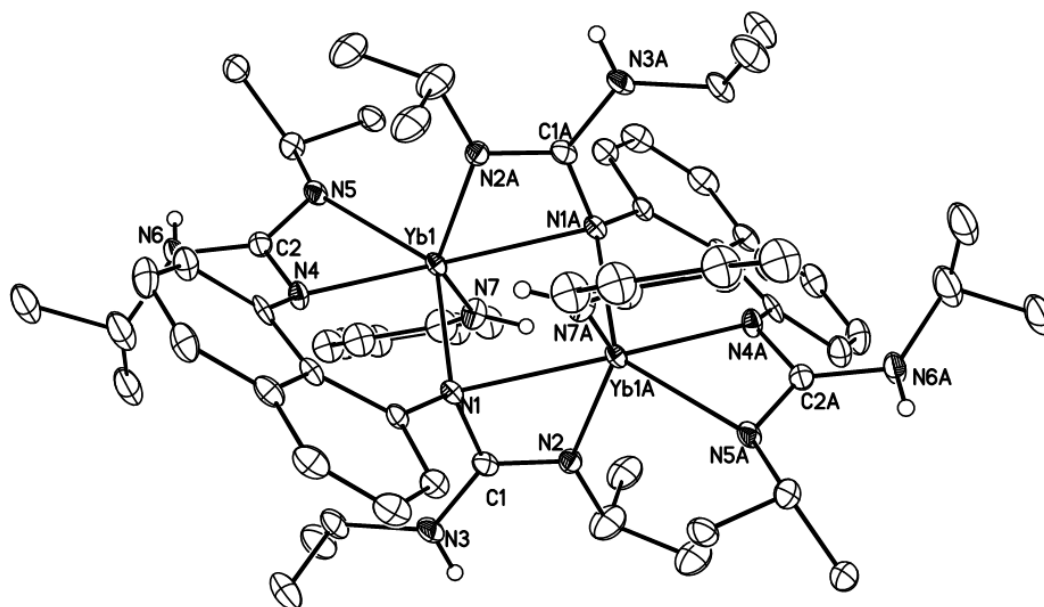
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Fig. 5 Molecular structure of complex **7**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those on the nitrogen atoms) and free THF molecule in the lattice are omitted for

10   clarity.

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Unprecedented reaction of bridged bis(guanidinate) lanthanide complexes: Sterically induced deprotonation

Chuanyong Wang, Xingmin Zhang, Mingqiang Xue,* Yong Zhang and Qi Shen*

Text:

Synthesis of bridged (mono- and dianionic)guanidinate lanthanide complexes by sterically induced deprotonation and their reactivity toward amines are described.

Graphic:

Ar = 4-ClC$_6$H$_4$, 4-CH$_3$C$_6$H$_4$