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Lanthanide–Alkali Metal Sandwich Complexes: Synthesis, Structure, and Solvent-Mediated Redox Transformations, and One-Dimensional Frameworks Assembled through Cation–Arene π Interactions

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The article "Lanthanide–Alkali Metal Sandwich Complexes: Synthesis, Structure, and Solvent-Mediated Redox Transformations, and One-Dimensional Frameworks Assembled through Cation–Arene π Interactions" by Cheng-Ling Pan, Xingwei Li, and Hongjie Zhang, published online on November 24, 2009 in Wiley Online Library (http://www.onlinelibrary.wiley.com/10.1002/chem.200901991) has been retracted (October 9, 2010) by the journal editor-in-chief, Dr. Neville Compton, and Wiley-VCH, in accordance with the "EUCheMS Ethical Guidelines for Publication in Journals and Reviews" adhered to by the journal (EUCheMS Ethical Guidelines for Publication in Journals and Reviews, 2006), due to lack of agreement among the authors regarding its publication.

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Lanthanide–Alkali Metal Sandwich Complexes: Synthesis, Structure, and Solvent-Mediated Redox Transformations, and One-Dimensional Frameworks Assembled through Cation–Arene π Interactions

Cheng-Ling Pan,[a] Xingwei Li,[b] and Hongjie Zhang*[a]

Abstract: Reaction of the potassium salt of amido ligand $[Ph_2Si(NAr)_2]^{2-}$ (L, Ar = 2,6-*i*$Pr_2C_6H_3$) and $LnI_2(thf)_2$ (Ln = Sm, Yb) gives sandwich complexes $[(L)_2Ln\{K(Et_2O)\}_2]$ (Ln = Sm (**2**), Yb (**3**)) with potassium–arene π interactions. Reaction of **2** with azobenzene gave the dimeric samarium cluster $[(L)_2Sm_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_2\{K(thf)_2\}_2]$ (**4**) and the tetrameric $[(L)Sm_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_3(\mu_3\text{-}NPh)_2(thf)_3]$ (**5**). On the other hand, the reaction of **2** with α-diimines ligands ArN=CRCR=NAr (DAD, R = H, Me) gives two Sm^{III} complexes: polymeric $[(L)Sm\{(ArN)RC{=}CR(NAr)\}K]_n$ (R = H (**6**), Me (**7**)) assembled through cation–π interactions and byproduct $[\{(L)_2Sm\}\{K(thf)_6\}]$ (**8**). Complexes **2–8** have been fully characterized by elemental analyses and X-ray crystallography. In particular, crystallographic analyses of **6** and **7** revealed that in both complexes samarium(III) is stabilized by dianionic DAD units.

Keywords: heterometallic complexes · N ligands · pi interactions · samarium · sandwich compounds

Introduction

Ever since Kagan et al. reported SmI_2 as a reagent for reductive coupling reactions in organic synthesis, the chemistry of lanthanide complexes has been increasingly attractive, yet it is dominated by samarium compounds that show the typical reactivity of divalent lanthanide complexes.[1] Considering the significant potential of a large pool of lanthanide(II) complexes as soluble one-electron reductants in organic and organometallic synthesis, it is somewhat surprising that to date most studies on lanthanide reactivity and transformation have been carried out for samarocene and its derivatives.[2] Nitrogen donors are commonly used to support lanthanides, and the significance of sterically encumbered amido ligands was first demonstrated in the isolation of homoleptic lanthanide(III) complex $[Ln\{N(SiMe_3)_2\}_3]$.[3] In the past years, there has been increasing interest in the development of various amido ligands for stabilizing lanthanide complexes, and rich chemistry has been demonstrated in terms of structures and reactivity.[4] The accessibility and applications of divalent lanthanide amido complexes as reductants can potentially be significantly broadened if they can be readily prepared.[5] Thus, the synthesis of a wide variety of lanthanide amido complexes remains an important task.

Chemical properties are always affected to some extent by the steric and electronic environments of the metal center. Therefore, desired reactivity and catalytic activity of lanthanide metal complexes might be achieved through careful ligand design. Hitchcock et al. have developed synthetic routes to bulky bis-amido ligands $[Ph_2Si(2,6\text{-}i\text{Pr}_2C_6H_3N)_2]^{2-}$ (L).[6] We reasoned that the ligating behavior of L could be comparable or close to those of bulky N,N′-chelating β-diketiminates $[\{(R^1)NC(R^2)\}_2CR^3]^-$ (nacnac$^-$)[7] and guanidinate ligands $[(ArN)_2CN(C_6H_{11})_2]^-$ (Giso$^-$).[8] These ligands are known to stabilize tetrahedral Ln(II) complexes.[7,8] We now expand their utilization to the stabilization of low oxidation state lanthanide (Ln = Sm and Yb) complexes. Metal imido complexes have been identified as key intermediates in both industrial and biological processes such as dinitrogen fixation.[9] Here we report the synthesis of well-characterized planar four-coordinate Ln^{II} bis-amido complexes $[(L)_2Ln\{K(Et_2O)\}_2]$ (Ln = Sm (**2**), Yb (**3**)), which are the first examples of lanthanide complexes with heterometallic sandwich structures. These bis-amido complexes react with azobenzene to give rare examples of samarium clusters $[(L)_2Sm_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_2\{K(thf)_2\}_2]$ (**4**) and $[(L)Sm_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_3(\mu_3\text{-}NPh)_2(thf)_3]$ (**5**) as a result of N=

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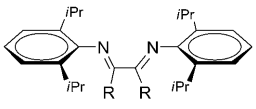
N bond cleavage. This reaction is possibly relevant to model studies of N_2 fixation in which N≡N bonds are reductively cleaved.

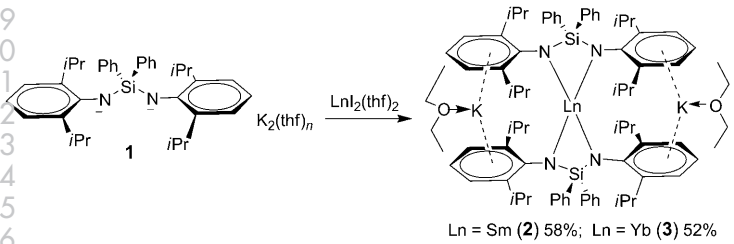
The use of lanthanide ions for construction of coordination polymers and oligomers is more difficult than using their d-block metal analogues.[10] The interaction between alkali metal cations and the π faces of neutral aromatic systems has emerged as an important binding force in a diverse range of biological and chemical settings.[11] The construction of lanthanide–alkali metal chains,[12] layers,[13] and wheels[14] with π interactions has been a field of rapid growth because of the formation of fascinating structures and their potential applications.[15] "Redox-active" 1,4-disubstituted diazabutadiene ligands (DAD) are advantageous for divalent lanthanide chemistry.[16] To gain insight into the redox reactivity of samarium towards sterically hindered DAD ligands (Scheme 1), we investigated the reaction of complex **2** and DAD and obtained one-dimensional frameworks with metal–arene π interactions $[(L)Sm\{(ArN)RC{=}CR(NAr)\}K]_n$ (R = H (**6**), Me (**7**)) and dimeric Sm^{III} by-product $[\{(L)_2Sm\}\{K(thf)_6\}]$ (**8**). Metal–π interactions are believed to play a key role in numerous biological recognition processes.[17]



Scheme 1. DAD ligands.

Results and Discussion

As illustrated in Scheme 2, $[(L)_2Ln\{K(Et_2O)\}_2]$ (Ln = Sm (**2**), Yb (**3**)) can be prepared in by treating amido salt **1** with the corresponding $LnI_2(thf)_2$ complex. X-ray crystallographic analysis revealed **2** and **3** to be heterometallic complexes with potassium ions between two pairs of phenyl rings that differ from homoleptic complexes with nacnac$^-$[7] and Giso$^-$[8] ligands. Both **2** and **3** adopt a four-coordinate, nearly planar geometry around the Ln^{II} center (Figure 1, Table 1). Over the past few years, there has been significant interest in lanthanide complexes with low coordination numbers (<6).[18] Here the coordination sphere includes two chelating L ligands. Two potassium ions are incorporated in each molecular unit. Each potassium ion is sandwiched between two phenyl rings with cation–arene π interactions. In addition to the π interactions with two arene rings, each potassium ion is further bound to a Et_2O molecule. The bis-amido ligands coordinate in a chelating fashion with Sm–N distances (Sm1–N1 2.547(2), Sm1–N2 2.550(2) Å) notably longer than those observed in related trivalent samarium amido species (e.g., 2.356(9)–2.367(9) Å in five-coordinate $[\{K(THF)_6\}_2\{Sm(\mu\text{-}NHC_6H_3Me_2\text{-}2,6)(NHC_6H_3Me_2\text{-}2,6)_3\}_2]$[19] and 1.18 and 0.96 Å for the ionic radii of Sm^{2+} and Sm^{3+} in six-coordinate complexes, respectively).[20] The K–C distances range from 3.032(3) to 3.456(3) Å, and the K1–O1 distance is 2.752(2) Å.



Scheme 2. Reaction of **1** with $LnI_2(thf)_2$ in a 2:1 molar ratio in THF.

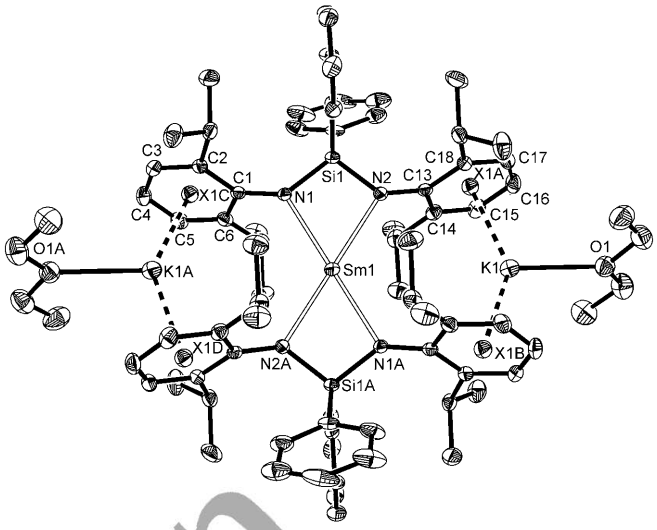


Figure 1. Molecular structure of **2** with all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1–N1 2.547(2), Sm1–N2 2.550(2), Si1–N1 1.693(2), Si1–N2 1.701 (2), K1–O1 2.752(2), K1–C14 3.222(3), K1–C16 3.077(3), K1–C17 3.094(3), K1–C15 3.114(3), K1–C18 3.168(3), K1–X1 A 2.829, K1–X1B 2.925; N1-Sm1-N1A 180.00(10), N2-Sm1-N2A 180.00(9), N1-Sm1-N2 63.32(7).

Table 1. Selected bond lengths [Å] and angles [°] for **2** and **3**.

	2 (Ln = Sm)	**3** (Ln = Yb)
Ln–N1	2.547(2)	2.424(2)
Ln–N2	2.550(2)	2.442(2)
Si1–N1	1.693(2)	1.703(2)
Si1–N2	1.701 (2)	1.696(2)
N1-Ln-N2	63.32(7)	66.32(7)
N1-Ln-N1A	180.00(10)	180.0
N2-Ln-N2A	180.00(9)	180.0

Divalent lanthanocenes $[(C_5Me_5)_2Ln]$ with sandwich structure have attracted considerable attention in the past few decades.[21] Evans et al. reported triple-decker bent metallocenes complexes of divalent lanthanides $[(\mu\text{-}\eta^8,\eta^8\text{-cot})\{Ln(C_5Me_5)_2\}_2]$ (cot = cyclooctatetraenyl).[22] Recently, Edelmann et al. reported a rare tetradecker sandwich complex of a divalent lanthanide, namely, $[(C_5Me_5)Yb(\mu\text{-}\eta^8,\eta^8\text{-cot}''')Yb(\mu\text{-}\eta^8,\eta^8\text{-cot}''')\ Yb(C_5Me_5)]$ (cot''' = 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl dianion).[23] Half-sandwich bistetramethylaluminate complexes of the rare earth metals were reported by Anwander et al.[24] Complexes with one,

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two, or three lanthanide centers can give different types of sandwich structures. However, M′MM′ heterotrimetallic sandwich complexes such as complexes **2** and **3** have not been reported in lanthanide chemistry.

Metal imido and hydrazido complexes are particularly interesting because of their postulated roles in catalysis, nitrogen fixation, and atom- and group-transfer processes.[9] We chose to synthesize this type of complex by reduction of azobenzene with a solution of **2** in THF (Scheme 3). Depending on the stoichiometry, the reaction led to dimeric Sm^{III} complex $[(L)_2Sm_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_2\{K(thf)_2\}_2]$ (**4**) or tetrameric $[(L)Sm_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_3(\mu_3\text{-}NPh)_2(thf)_3]$ (**5**).

Our objective was to prepare a bridging hydrazine complex of Sm^{III} (e.g., $[Sm_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)]$) while maintaining the chelating amido ligands, by following the strategy developed by Evans and co-workers, that is, introduction of a $(PhNNPh)^{2-}$ group by transformation of azobenzene.[25] Reaction of azobenzene and two equivalents of **2** in thf at room temperature led to the formation of heterotetranuclear complex $[(L)_2Sm_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2Ph_2)_2\{K(thf)_2\}_2]$ (**4**).

As shown in Figure 2, the Sm atoms are each chelated by a bis-amido ligand and bridged by two $\eta^2\text{:}\eta^2\text{-}(PhNNPh)^{2-}$ units resulting from two-electron reduction of one azobenzene unit. Two potassium ions are each located between two phenyl rings. The Sm1–N1 and Sm1–N2 distances are 2.338(5) and 2.437(5) Å, respectively. The N3–N4A and N4–N3A distances of 1.448(7) Å are in line with the N–N single-bond range. The bridging hydrazine ligands coordinate in a unique fashion and lead to two distinct Sm–N distances. The Sm–N distance of 2.336 Å (av) is in the range expected for a Sm^{III}–NR_2 unit. The Sm–N distance of 2.699 Å (av) is in the range of $Sm^{III}\leftarrow\text{:}NR_3$ dative bonds. The K–C distances range from 3.043(12) to 3.351(7) Å, and K–O distances are 2.636 Å (av).

Single crystals of **5** were obtained from toluene, and each formula unit contains three molecules of toluene. The tetranuclear samarium cluster (Figure 3) has a bridging bis-amido ligand, three $\eta^2\text{:}\eta^2$-bridging $(PhNNPh)^{2-}$ units, and two μ_3-bridging imido NPh^{2-} groups resulting from two- and four-electron reduction of azobenzene, respectively. The overall $[Sm_4(\mu_3\text{-}NPh)_2]$ framework may be conveniently visualized as a face-sharing ditetrahedral structure in which

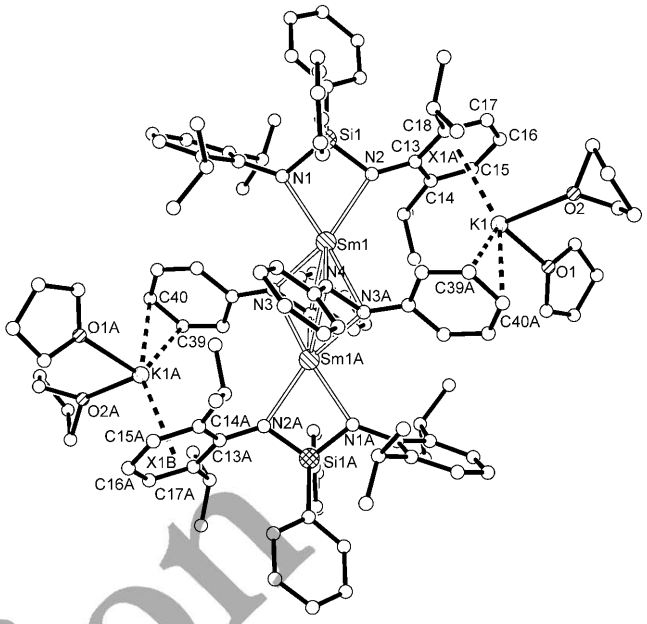
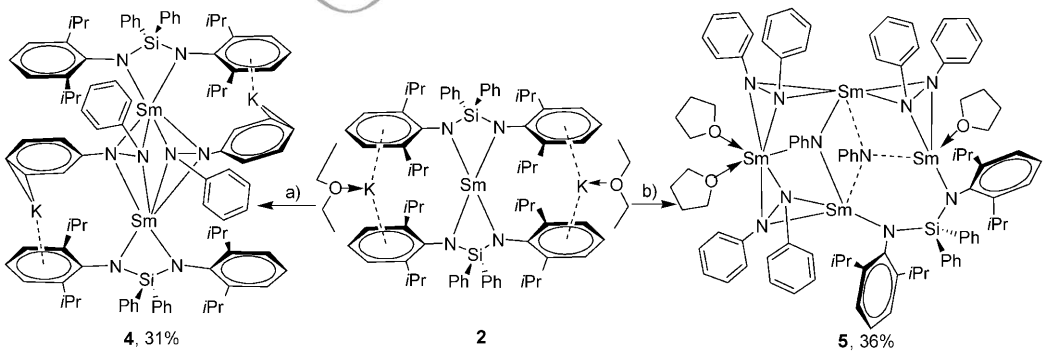


Figure 2. Molecular structure of **4** with all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1–N1 2.338(5), Sm1–N2 2.437(5), Sm1–N3 2.350(5), Sm^{1}A–N3 2.690(6), Sm1–N4A 2.709(5), Sm1–N4 2.322(5), K1–O1 2.611(7), K1–O2 2.611(12), K1–X1A 2.856; N1-Sm1-N2 66.93(18), N4-Sm1-N3A 32.54(17), N3-Sm1-N4A 32.28(17).

four Sm atoms form the basal plane and the nitrogen atoms of NPh^{2-} occupy the apical positions. The anionic ligands here can flexibly adopt different modes of ligation such as imido, hydrazido, and amido, which should impart a rich diversity of structures, reactivity and physicochemical properties for this complex. To the best of our knowledge, it is rare in lanthanide chemistry to have this type of bis-amido ligands in a bridging fashion without any short metal–metal bonds.[26] Moreover, a lanthanide complex with three different N-based ligands, such as imide, amide, and hydrazine, would be of great interest.

The N–N distances of 1.469(9), 1.471(9), and 1.467(9) Å in the PhNNPh units of **5** have N–N single-bond nature and are in line with those observed for **4**. The Sm–N distances (Sm3–N3 2.372(6), Sm1–N4 2.308(6), Sm3–N5 2.392(7), Sm4–N6 2.341(7), Sm2–N7 2.360(7), Sm4–N8 2.310(7) Å)



Scheme 3. Reaction **2** with PhN=NPh in a) 2:1 and b) 3:1 molar ratio in THF at room temperature.

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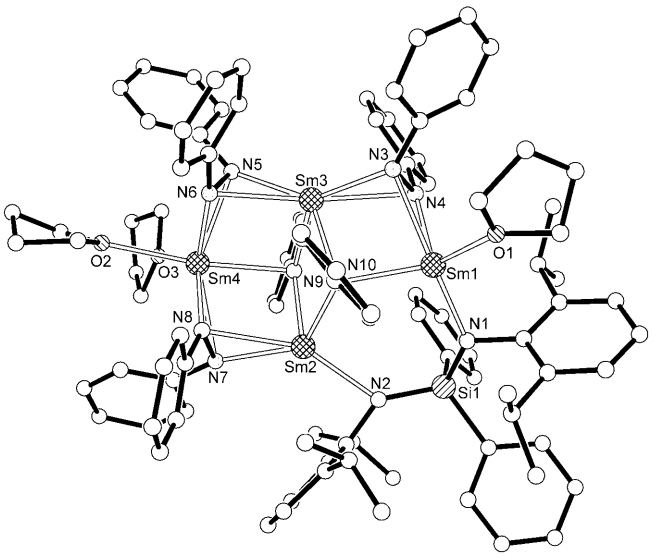


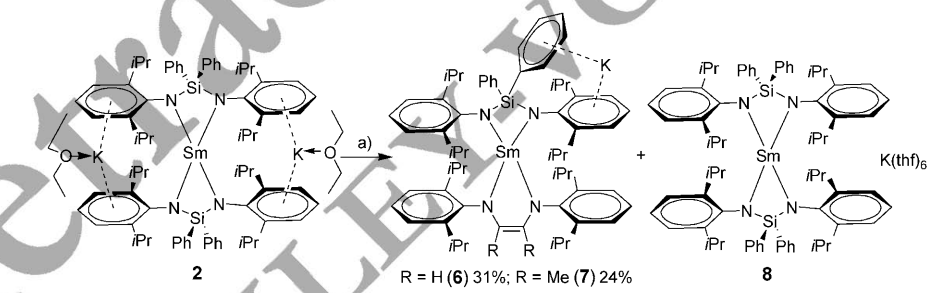
Figure 3. Molecular structure of **5** with all hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Sm1–N1 2.287(6), Sm2–N2 2.356(6), Sm1–N3 2.522(7), Sm1–N4 2.308(6), Sm3–N3 2.372(6), Sm3–N4 2.598(7), Sm3–N5 2.392(7), Sm3–N6 2.524(7), Sm4–N5 2.502(7), Sm4–N6 2.341(7), Sm4–N7 2.558(7), Sm4–N8 2.310(7), Sm2–N7 2.360(7), Sm2–N8 2.576(7), Sm2–N9 2.289(7), Sm3–N9 2.351(6), Sm4–N9 2.471(6), Sm2–N10 2.327(6), Sm1–N10 2.339(6), Sm3–N10 2.460(6), N9···N10 2.928.

are in the range expected for a Sm^{III}–NR_2 unit on the basis of the data measured for complex **4** , whereas the Sm–N distances for Sm1–N3 2.522(7), Sm3–N4 2.598(7), Sm4–N5 2.502(7), Sm3–N6 2.524(7), Sm4–N7 2.558(7), and Sm2–N8 2.576(7) Å are in the range expected for a Sm^{III}←:NR_3 dative bond. These data show that each PhNNPh group forms two covalent single bonds with neighboring Sm atoms and two dative bonds with two other Sm atoms. The Sm–N distances of the μ_3-NPh units range from 2.289(7) to 2.460(6) Å.

Cleavage of the N=N bond of azobenzene has been observed in divalent lanthanide chemistry.[25,27] Here azobenzene cleavage gave a well-defined imido samarium cluster. In comparison with the limited examples of complexes of d-block transition metal such as those of Group 4[29] or polyoxometalates with organic imido ligands[30], lanthanide imido and amido complexes have been much less studied, and examples of organolanthanide clusters containing imido groups are even rarer. In the lanthanide series, NR^{2-} groups act as bridging and capping ligands in di-, tetra-, and hexanuclear compounds,[27,28] and this binding versatility can lead to a diversity of structures, reactivity, and physicochemical properties.

Owing to the redox properties and the lower lying π* orbital of DAD ligands, their samarium complexes, which typically have a very low potential of the Sm^{II}/Sm^{III} couple, are of particular interest for intramolecular metal-to-ligand electron transfer.[31] Indeed, addition of 0.5 equivalents of DAD to complex **2** in THF caused a color change to dark yellow (Scheme 4).

X-ray analyses revealed that **6** and **7** are heterodinuclear complexes, the tetrahedral coordination spheres of which include two N,N chelating ligands (Figure 4, Table 2). The bond lengths within the DAD moieties of **6** and **7** indicate dianionic character, and this is evidenced by elongation of the C–N bond and shortening of the C–C bond of the NCCN unit of DAD.[28] Here two electrons transfer from Sm to the LUMO of the DAD ligand. In contrast to the N=C (1.267(2) Å) and C–C bond lengths (1.467(2) Å) in the free DAD molecule,[32] the N–C bonds in the DAD ligands of **6** (1.410(3) and 1.411(3) Å) and **7** (1.425(4) and 1.424(3) Å) are substantially elongated, whereas the C–C bonds (**6**: 1.358(4) Å, **7**: 1.377(5) Å) are shortened and close to the values of typical C=C double bonds. The one-dimensional frameworks are assembled through cation–arene π interactions with K–C distances ranging from 3.077(3) to 3.513(2) Å in **6**, and from 3.015(4) to 3.534(3) Å in **7**. The cation bridges the metalate units by π coordination to aromatic rings, and thus wheel-shaped coordination oligomers are formed with K–C interactions up to 3.5 Å.[14a]



Scheme 4. Reaction **2** with DAD ligands in 2:1 molar ratio at room temperature.

Further analysis of the packing pattern of **6** and **7** shows that they form a one-dimensional framework. This emphasizes the unusual properties of lanthanide amide DAD complexes as π linkers to bridge preformed alkali metal aggregates. We became interested in cation–π interactions during our recent work on incorporating f-block metals into metal–organic frameworks. Here we successfully demonstrated that f-block metal aggregates may be linked through ditopic Lewis base linkers to form one-dimensional networks, as shown in Figure 5 for complex **6**. Formation of coordination polymers through a combination of unsaturated K centers and polytopic donor ligands has been one of the most successful strategies adopted in the preparation of extended structures.

X-ray analysis also revealed the molecular structure of trivalent cationic Sm complex **8**. In sharp contrast to complex **2**, oxidation of Sm^{II} to Sm^{III} gave a distorted tetrahedral ge-

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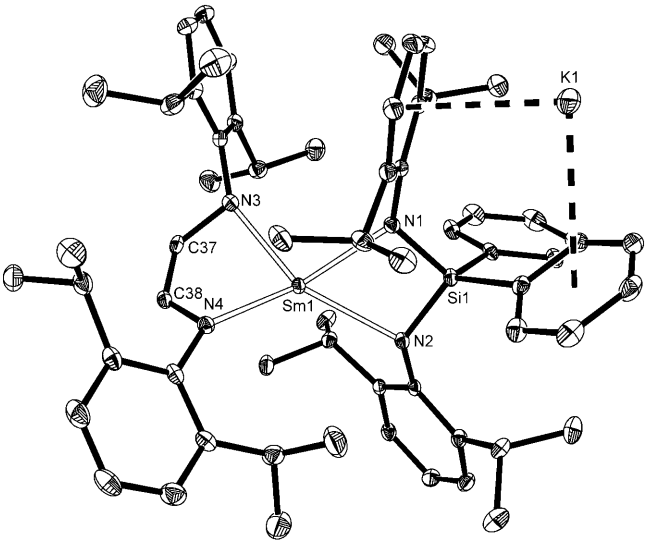

Figure 4. Molecular structure of **6** with all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1–N1 2.333(2), Sm1–N2 2.454(2), Sm1–N3 2.250(2), Sm1–N4 2.285(2), Sm1–C37 2.707(2), Sm1–C38 2.726(2); N1-Sm1-N2 66.15(7), N3-Sm1-N4 81.91(8).

Table 2. Selected bond lengths [Å] and angles [°] for **6** and **7**.

	6	**7**
Sm1–N1	2.333(2)	2.344(3)
Sm1–N2	2.454(2)	2.489(3)
Sm1–N3	2.250(2)	2.248(3)
Sm1–N4	2.285(2)	2.257(3)
Sm1–C37	2.707(2)	2.703(3)
Sm1–C38	2.726(2)	2.731(3)
C37–C38	1.358(4)	1.377(5)
N4–C38	1.411(3)	1.425(4)
N3–C37	1.410(3)	1.424(4)
N3-Sm1-N4	81.91(8)	80.99(10)
N1-Sm1-N2	66.15(7)	66.04(9)

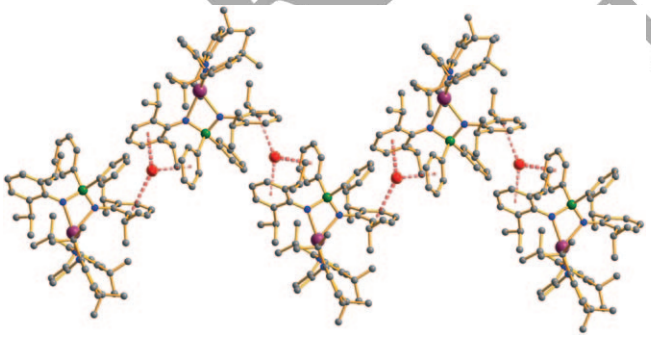

Figure 5. Extended section of **6** showing the zigzag polymeric chain structure. Hydrogen atoms are omitted for clarity.

ometry around the metal center (Figure 6). The Sm1–N1 and Sm1–N2 distances are 2.308(4) and 2.350(4) Å, respectively, and the N-Sm-N' angles are 68.14(13)°. The potassium anion is coordinated by six THF molecules with K–O distances ranging from 2.655(4) to 3.319(8) Å.

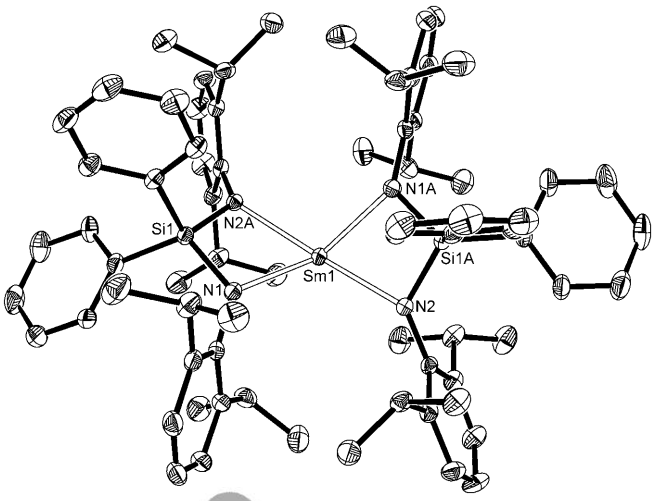

Figure 6. ORTEP (30% probability thermal ellipsoids) of the $[(L)_2Sm]^-$ ion of **8** showing the numbering scheme for non-hydrogen atom. Selected bond lengths [Å] and angles [°]: Sm1–N1 2.308(4), Sm1–N2 2.350(4), N1–Si1 1.714(4), N1–Sm1–N2A 68.14(13), N1–Sm1–N1A 128.59(19), N2-Sm1-N2A 170.71(17).

The Sm^{III}–N distances in **8** are shorter than the corresponding Sm^{II}–N bond distances in **2** by at least 0.2 Å. In addition, the N-Sm^{III}-N' bite angles in this Sm^{III} complex are larger than the corresponding N-Sm^{II}-N' bite angles in the Sm^{II} precursor, probably due to the difference in radii of the Sm centers. To further explore the coordination chemistry of the present bis-anionic amido ligands towards Sm^{II}, we attempted to synthesize the corresponding Sm^{II} compound by treating $SmI_2(thf)_2$ with one equivalent of potassium amide **1**. However, essentially no divalent Sm complex was isolable. Instead, the corresponding trivalent samarium complex **8** was obtained at room temperature in high yield. Here the potassium cation is likely abstracted by excess iodide ligand, which further confirms the significance of cation–π interactions in stabilizing the divalent lanthanide metal centers.

Conclusions

The careful choice of ligands, metal-to-ligand ratio, and solvent system allowed the isolation of divalent lanthanide complexes. In the unique structures of complexes **2** and **3** potassium ions are sandwiched between two phenyl rings and serve to stabilize the divalent metal center. Synthesis of imido and hydrazido complexes by Sm^{II}-mediated reductive cleavage of azobenzene has been successfully achieved, yielding nitrogen-bridged lanthanide clusters. In addition, an unusual redox reaction between a samarium bis-amide and DAD ligands gave complexes with one-dimensional networks assembled through cation–π interactions. Our studies confirm that heteroleptic sandwich complexes of lanthanides with bis-amide ligands can be used as ditopic linkers to create network structures by way of cation–π interaction. The structural versatility and novelty of these samarium

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compounds are an incitement to further investigate the reactivity of lanthanide compounds. We believe that this method should be applicable for the synthesis of complexes of other lanthanide elements, and this work is in progress in our laboratory and will be reported in due course.

Experimental Section

General remarks: All procedures were performed under vacuum by using standard Schlenk techniques or in a nitrogen-filled dry-box. THF was pre-treated with KOH and then distilled from sodium benzophenone ketyl prior to use. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or CaH_2. All other commercially available chemicals were used after appropriate purification. NMR spectra were recorded on a Bruker DPX 300 spectrometer. Elemental analyses (C, H, N) were carried out in the microanalytical laboratory of the Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences.

X-ray crystallography: Crystals were examined under polybutene/polyisobutylene oil. The datum crystal was affixed to a thin glass fiber mounted atop a tapered copper mounting pin and transferred to the 100 K nitrogen stream of a Bruker APEX II diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Table 3 lists the key crystallographic parameters for **2**–**8**. The intensity data were integrated by means of the SAINT program.[33] SADABS[34] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and refined against F^2 using all reflections with the aid of the SHELXTL package.[35] Structures were solved by direct methods. Non-hydrogen atoms not present in the direct-methods solution were located by successive cycles of full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at idealized geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 times the equivalent isotropic U value of the parent atom, and to 1.5 U for methyl hydrogen atoms. CCDC-716920 (**2**), CCDC-721697 (**3**), CCDC-716921 (**4**), CCDC-716922 (**5**), CCDC-721698 (**6**), CCDC-721699 (**7**), and CCDC-721700 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1: A solution of $[Ph_2Si(2,6\text{-}i Pr_2C_6H_3NH)_2]$[6] (3.2 g, 6 mmol) in THF (20 mL) was slowly added to a stirred suspension of KH (0.32 g, 8 mmol) in THF. The resulting mixture was stirred for 8 h and then filtered to remove any insoluble material. The yellow solution obtained was concentrated to about 2 mL and hexane (5 mL) was added. The resulting solution was then concentrated to about 2 mL and left at room temperature for three days to give compound **1** as colorless crystals (3.32 g, 73%). ^{1}H NMR (C_7D_8, 300 MHz): $\delta = 7.86$ (d, $J = 6.6$ Hz, 2H, ArH), 7.12–7.20 (m, 10H, ArH), 6.97–6.99 (m, 2H, ArH), 6.75 (t, $J = 7.5$ Hz, 2H, ArH), 4.20 (sept, $J = 6.3$ Hz, 4H, C*H*Me$_2$), 2.92–3.03 (m, 4H, THF), 1.17–1.13 (m, 4H, THF), 1.17 ppm (d, $J = 6.3$ Hz, 24H, CH*Me*$_2$); ^{13}C{^{1}H} NMR (C_7D_8, 75.47 MHz): $\delta = 142.8$, 135.5, 127.0, 123.5, 115.7 (Ar), 68.2, 23.6 (OCH$_2$CH$_2$ (THF)), 29.27 (CHMe$_2$), 24.76 ppm (CHMe$_2$); elemental analysis (%) calcd for $C_{40}H_{52}K_2N_2OSi$: C 70.33, H 7.67, N 4.10; found: C 70.71, H 8.38, N 4.46.

Synthesis of 2: THF (30 mL) was added to a mixture of $SmI_2(thf)_2$ (0.90 g, 1.61 mmol) and $[Ph_2Si(NAr)_2K_2(thf)]$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; 2.25 g, 3.0 mmol) to give a blue suspension. This mixture was stirred for a while, resulting in a rapid color change to purple with concomitant formation of a white precipitate (KI). After 6 h the precipitate was separated by filtration, and the intensely purple filtrate was reduced to dryness to afford a purple oil, which slowly crystallized on standing at room temperature.

Table 3. Selected crystal data for **2**–**8**.

	2	**3**	**4**	**5**·3C$_7$H$_8$	**6**	**7**·Et$_2$O	**8**
formula	$C_{80}H_{108}K_2N_4O_2Si_2Sm$	$C_{80}H_{108}K_2N_4O_2Si_2Yb$	$C_{112}H_{140}K_2N_8O_4Si_2Sm_2$	$C_{117}H_{132}N_{10}O_3SiSm_4$	$C_{62}H_{80}KN_4SiSm$	$C_{68}H_{94}KN_4OSiSm$	$C_{96}H_{136}KN_4O_6Si_2Sm$
M_r	1442.44	1465.12	2097.40	2355.82	1098.87	1201.04	1687.72
crystal system	Monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	tetragonal
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P4_2/n$
a [Å]	12.2917(7)	12.3080(9)	13.8271(7)	14.1516(12)	14.0691(5)	15.1405(6)	27.8688(4)
b [Å]	22.2862(13)	22.0720(15)	20.2272(10)	17.8697(15)	18.4893(6)	17.3825(7)	27.8688(4)
c [Å]	15.2764(8)	15.1387(10)	18.5263(10)	20.9102(19)	24.9718(8)	25.3515(10)	23.5200(7)
α [°]	90	90	90	86.765(2)	90	90	90
β [°]	113.4650(10)	113.3840(10)	95.6610(10)	87.113(2)	92.1200(10)	95.0880(10)	90
γ [°]	90	90	90	82.2270(10)	90	90	90
V [Å^3]	3838.7(4)	3774.8(5)	5156.2(5)	5226.1(8)	6491.4(4)	6645.7(5)	18267.3(7)
Z	4	4	4	2	4	4	8
ρ [Mg m^{-3}]	1.248	1.289	1.351	1.497	1.141	1.176	1.227
$u(Mo_{K\alpha})$ [mm^{-1}]	0.951	1.428	1.287	2.282	1.025	1.004	0.768
crystal size [mm]	0.30×0.20×0.10	0.40×0.30×0.20	0.30×0.30×0.20	0.30×0.20×0.20	0.42×0.35×0.26	0.41×0.37×0.25	0.31×0.26×0.19
θ range [°]	1.72–26.03	1.73–26.21	1.49–26.04	0.98–26.12	1.37–26.09	1.35–26.10	1.03–25.90
max./min. transmission	0.9109/0.7635	0.7633/0.5989	0.7829/0.6988	0.6582/0.5476	0.7765/0.6728	0.7873/0.6835	0.8678/0.7968
reflns collected	21099	21051	28206	29185	35946	36742	100166
independent reflns	7540	7563	10135	20432	12877	13188	17761
observed reflns [$I > 2\sigma(I)$]	412	407	561	1152	622	685	987
GOF on F^2	1.019	1.025	1.065	1.034	0.997	1.068	1.026
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0370, 0.0777	0.0326, 0.0731	0.0601, 0.1499	0.0544, 0.1308	0.0302, 0.0737	0.0358, 0.1071	0.0506, 0.1389
$R1$, wR2 (all data)	0.0619, 0.0863	0.0460, 0.0781	0.0933, 0.1730	0.0882, 0.1562	0.0403, 0.0772	0.0456, 0.1163	0.0978, 0.1735
largest peak/hole [e Å^{-3}]	0.444/−0.296	0.579/−0.406	3.676/−1.893	1.573/−1.021	0.469/−0.381	1.229/−0.537	2.788/−1.042

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Recrystallization from Et_2O (ca. 25 mL) afforded **2** as purple-black crystals (1.25 g; 58%). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.78, 7.22–7.12 (32H, ArH), 3.44 (8H, C*H*Me$_2$), 1.24 (48H, CH*Me*$_2$), 2.25, 1.04 ppm (20H, Et_2O); IR (KBr): $\tilde{\nu}$ = 1590 (w), 1460 (m), 1438 (s), 1427 (m), 1381 (m), 1361 (m), 1307 (w), 1252 (m), 1196 (m), 1154 (w), 1109 (s), 1105 (w), 1042 (w), 998 (w), 913 (m), 899 (m), 877 (w), 777 (m), 762 (w), 739 (m), 700 (m), 650 (w), 593 (w), 543 (w), 511 (w), 488 cm^{-1} (m); elemental analysis (%) calcd for $C_{80}H_{108}K_2N_4O_2Si_2Sm$: C 66.61, H 7.55, N 3.88; found: C 66.77, H 7.68, N 3.44.

Synthesis of 3: A similar procedure to that for **2** was followed for preparation of **3**. Recrystallization from Et_2O (ca. 30 mL) afforded **3** as green block crystals (1.09 g; 52%). ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.70 (d, J = 3 Hz, 8H, ArH), 7.13–7.18 (m, 12H, ArH), 7.09 (s, 12H, ArH), 2.35, 1.05 (20H, Et_2O), 3.35 (sept, J = 6.6 Hz, 8H, C*H*Me$_2$), 0.98 ppm (d, J = 6.6 Hz, 48H, CH*Me*$_2$);. ^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz): δ = 143.1, 139.8, 135.8, 130.4, 124.1, 123.4 (Ar), 68.1, 66.2, 29.4, Et_2O), 26.1, 23.9, 22.9, 15.9 ppm (ArCHMe$_2$); IR (KBr): $\tilde{\nu}$ = 1590 (m), 1597 (w), 1460 (m), 1438 (s), 1427 (s), 1381 (m), 1361 (m), 1347 (w), 1332 (m), 1307 (w), 1264 (m), 1252 (m), 1196 (m), 1157 (w), 1114 (s), 1108 (s), 1055 (w), 1042 (m), 997 (w), 959 (w), 913 (m), 899 (m), 877 (w), 814 (w), 793 (w), 780 (m), 763 (m), 739 (m), 710 (w), 700 (s), 685 (w), 652 (w), 628 (w), 592 (w), 561 (w), 542 (w), 512 (m), 488 cm^{-1} (m); elemental analysis (%) calcd for $C_{80}H_{108}K_2N_4O_2Si_2Yb$: C 66.58, H 7.43, N 3.82; found: C 66.12, H 7.24, N 3.39.

Synthesis of 4: Compound **2** (1.45 g, 1.0 mmol) and azobenzene (0.09 g, 0.5 mmol) were stirred in THF (10 mL) for 4 h. The reaction mixture changed immediately from deep violet to a homogeneous bright yellow solution, indicating that the Sm^{II} compound was oxidized to the corresponding Sm^{III} complex. Recrystallization from Et_2O (ca. 10 mL) afforded 0.32 g (31%) of **4** as orange crystals. ^{1}H NMR (C_6D_6, 400 MHz) for **4**: δ = 7.81–7.00 (52H, ArH), 3.48 (8H, C*H*Me$_2$), 3.66, 1.52 (32H, thf), 1.10 (48H, CH*Me*$_2$); IR (KBr): $\tilde{\nu}$ = 1590 (m), 1460 (m), 1438 (s), 1427 (m), 1381 (m), 1361 (m), 1332 (m), 1307 (w), 1266 (m), 1252 (m), 1197 (m), 1157 (w), 1108 (s), 1055 (w), 1043 (m), 997 (w), 913 (s), 899 (s), 877 (m), 814 (w), 793 (m), 780 (m), 739 (s),700 (s), 628 (w), 593 (w), 561 (w), 512 (m), 488 cm^{-1} (m); elemental analysis (%) calcd for $C_{112}H_{140}K_2N_8O_4Si_2Sm_2$: C 64.3 H 6.73, N 5.34; found: C 63.98, H 6.49, N 5.21.

Synthesis of 5: Azobenzene (0.07 g, 0.38 mmol) was added to a THF solution of compound **2** (1.46 g, 1.0 mmol). Recrystallization from toluene (ca. 5 mL) afforded 0.21 g (36%) of **5**·3C_7H_8 as yellow crystals. ^{1}H NMR (C_6D_6, 400 MHz) for **5**: δ = 8.12–7.09 (56H, ArH), 3.48 (4H, C*H*Me$_2$), 3.67, 1.51 (24H, thf), 1.09 (24H, CH*Me*$_2$); IR (KBr): $\tilde{\nu}$ = 1590 (w), 1460 (m), 1438 (s), 1428 (m), 1382 (m), 1361 (m), 1332 (m), 1307 (w), 1252 (m), 1197 (m), 1154 (w), 1109 (s), 1055 (w), 1042 (m), 998 (w), 913 (s), 899 (s), 877 (m), 777 (m), 763 (w), 739 (s), 701 (s), 652 (w), 628 (w), 593 (w), 544 (w), 512 (w), 489 cm^{-1} (m); elemental analysis (%) calcd for $C_{96}H_{108}N_{10}O_3SiSm_4$ (three toluene molecules lost): C 55.45, H 5.23, N 6.74; found: C 56.02, H 5.48, N 6.31.

Synthesis of 6: Compound **6** was prepared by reaction of **2** (1.45 g, 1.0 mmol) and a 1,4-disubstituted diazabutadiene (DAD) ligand (0.19 g, 0.5 mmol) in THF. After the addition of DAD to the solution of **2**, the reaction mixture changed immediately from deep violet to a homogeneous black solution. The solution was stirred for 4 h, 0.35 g of **6** (31% based on Sm) was obtained as purple crystals from a concentrated Et_2O solution at room temperature. ^{1}H NMR (C_6D_6, 400 MHz) for **6**: δ = 7.83, 7.25–7.13 (22H, ArH), 3.50, 3.39 (8H, C*H*Me$_2$), 1.34, 1.25 (48H, CH*Me*$_2$) 1.16 (2H, NC*H*=C); IR (KBr): $\tilde{\nu}$ = 1625 (m), 1590 (w), 1460 (s), 1438 (s), 1429 (w), 1383 (m), 1363 (m), 1329 (m), 1255 (m), 1194 (w), 1179 (w), 1160 (w), 1111 (m), 1058 (w), 1044 (w), 998 (w), 914 (m), 878 (w), 796 (m), 763 (m), 739 (w), 701 (s), 685 (w), 595 (w), 571 (w), 491 cm^{-1} (m); elemental analysis (%) calcd for $C_{62}H_{80}KN_4SiSm$: C 66.77, H 7.34, N 5.10; found: C 65.92, H 7.09, N 4.96.

Synthesis of 7: A procedure similar to that for **6** was followed for preparation of **7**. Recrystallization from Et_2O (ca. 20 mL) afforded 0.29 g (24.2%) of **7**·Et_2O as purple block crystals; elemental analysis (%) calcd for $C_{64}H_{84}KN_4SiSm$ (one Et_2O of solvation lost): C 68.21, H 7.51, N 4.97%; found: C 67.47, H 7.54, N 4.23%. ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.81, 7.26–7.16 (22H, ArH), 3.50 (8H, C*H*Me$_2$), 1.34, 1.11 (54H, C*H*$_3$, CH*Me*$_2$, =CMe); IR (KBr): $\tilde{\nu}$ = 1642 (m), 1590 (m), 1460 (s), 1438 (s), 1428 (s), 1382 (m), 1363 (s), 1332 (m), 1254 (m), 1197 (m), 1159 (w), 1115 (m), 1109 (m), 1057 (w), 1043 (m), 997 (w), 959 (w), 933 (m), 913 (m), 899 (m), 877 (w), 816 (w), 793 (m), 781 (m), 763 (m), 739 (m), 710 (w), 700 (m), 686 (w), 628 (w), 593 (w), 562 (w), 513 (w), 489 cm^{-1} (w).

Synthesis of 8: Yellow crystals of complex **8** were obtained from a hexane/THF (5/1) (0.18 g, 10.2% based on Sm). ^{1}H NMR (C_6D_6, 400 MHz) for **8**: δ = 7.81, 7.26–7.15 (32H, ArH), 3.50, 3.37(8H, C*H*Me$_2$), 3.67, 1.53 (16H, thf), 1.09 ppm (48H, CH*Me*$_2$); IR (KBr): $\tilde{\nu}$ = 1619 (w), 1590 (m), 1460 (s), 1438 (s), 1428 (s), 1381 (m), 1361 (m), 1332 (m), 1308 (w), 1262 (m), 1253 (m), 1197 (m), 1157 (w), 1108 (s), 1055 (w), 1043 (m), 997 (w), 913 (m), 899 (m), 877 (w), 793 (m), 780 (m), 763 (w), 739 (s), 700 (s), 628 (w), 593 (w), 562 (w), 512 (w), 488 cm^{-1} (m); elemental analysis (%) calcd for $C_{80}H_{104}KN_4O_2Si_2Sm$ (4THF lost): C 68.67, H 7.49, N 4.00; found: C 69.06, H 7.59, N 3.87.

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