# A New Type of Lanthanide Complex – Two Divalent Ytterbium Species Assembled from Cation– $\pi$ Interactions

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A new divalent ytterbium complex,  $[\{(L^{\rm Ph})Yb^{\rm II}(Et_2O)(thf)\}_2(\mu-KI)]$   $\{L^{\rm Ph}$  =  $Ph_2Si(NAr)_2$ , Ar = 2,6- $iPr_2C_6H_3\}$  (3), was synthesized by the reaction of  $[(L^{\rm Ph})Yb^{\rm III}I(thf)_2]$  (2) and an excess of potassium. The bimetallic ytterbium(II) species with bulky

#### Introduction

Ever since Kagan's report on SmI<sub>2</sub>, the chemistry of lanthanide complexes has been increasingly attractive. However, the chemistry of divalent lanthanide complexes is largely limited, because of destabilizing factors.<sup>[1]</sup> For a long time, the coordination chemistry of divalent lanthanide ions has been limited to that of the classical three elements  $Eu^{2+}$ , Yb<sup>2+</sup>, and Sm<sup>2+</sup>.<sup>[2]</sup> These Ln<sup>2+</sup> ions have the configuration of  $6s^{0}5d^{0}4f^{n}$ , with n = 6 (Sm), 7 (Eu), and 14 (Yb). The reduction potentials for the trivalent ions  $Ln^{3+} + e^- = Ln^{2+}$ are Eu<sup>3+</sup>/Eu<sup>2+</sup> (-0.35 V), Yb<sup>3+</sup>/Yb<sup>2+</sup> (-1.15 V), and Sm<sup>3+</sup>/  $Sm^{2+}$  (-1.55 V), similar to those of one-electron reducing agents in organic and inorganic synthesis.<sup>[3]</sup> In contrast, the reduction potential for potassium is much more negative [K/K<sup>+</sup> (-2.92 V)].<sup>[4]</sup> Therefore, with a properly useful ligand, we should be able to stabilize these ions with oxidation state +2 in solution by alkali metal reduction of their trivalent precursors. However, the synthesis of a wide variety of low-valent lanthanide complexes with N,N'ligands remains sparsely studied.<sup>[5]</sup>

The accessibility and applications of divalent lanthanide complexes can potentially be significantly broadened if they can be readily prepared.<sup>[6–9]</sup> In addition to the success in their synthesis, it is still important to explore alternative ligands that are able to satisfy the coordination requirements of relatively large lanthanide cations.<sup>[10,11]</sup> In contrast to the popular cyclopentadienyl (Cp) ligands, relatively little effort has been devoted to Cp-free ligands.<sup>[12]</sup> The lanthanide chemistry of complexes with simple amido ligands is limited primarily to an amido ligand, namely

[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China E-mail: mrfy@jlu.edu.cn diamido ligands are bridged by a KI molecule with cation- $\pi$  interactions. These two complexes have been fully characterized, particularly by X-ray crystallography.

N(SiMe<sub>3</sub>)<sub>2</sub>.<sup>[13,14]</sup> In this respect, it is noteworthy that the stabilizing properties of  $L^{Ph}$  [ $L^{Ph}$  = Ph<sub>2</sub>Si(NAr)<sub>2</sub>, Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] appear to be similar to those of bulky, *N*,*N'*-chelating  $\beta$ -diketiminates [{(R<sup>1</sup>)NC(R<sup>2</sup>)}<sub>2</sub>C(R<sup>3</sup>)]<sup>-</sup> (nacnac<sup>-</sup>)<sup>[15,16]</sup> and guanidinate ligands [(ArN)<sub>2</sub>CN-(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup> (Giso<sup>-</sup>),<sup>[17]</sup> which have been utilized in the preparation and characterization of homoleptic four-coordinate Ln<sup>2+</sup> complexes.

In our previous work, we obtained planar four-coordinate  $Ln^{II}$  diamido complexes  $[(L^{Ph})_2Ln \{K(solv.)_x\}_2]$  (Ln = Sm, Yb, and Eu), which represent the first example of lanthanides bearing heteroleptic sandwich structures.<sup>[18–19]</sup> These results inspired us to extend the coordination chemistry of bulky diamido ligands to ytterbium(II) by taking advantage of related synthetic routes and cation– $\pi$  interactions. We have explored the coordination of amido ligand  $H_2(L^{Ph})^{[20]}$  [ $L^{Ph} = Ph_2Si(NAr)_2$ ,  $Ar = 2,6 \cdot iPr_2C_6H_3$ ] (1) to stabilize the ytterbium(II) complex, [ $\{(L^{Ph})Yb^{II}$  (thf)-(Et<sub>2</sub>O) $\}_2(\mu$ -KI)] (3), by the reaction of [ $(L^{Ph})Yb^{III}$ I(thf)2] (2)



Scheme 1.

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and an excess of potassium, as illustrated in Scheme 1. Herein, we report the synthesis and structural studies of these complexes. To the best of our knowledge, ytterbium(II) dimer complexes of amido ligands assembled from cation– $\pi$  interactions are rare in lanthanide chemistry.

### **Results and Discussion**

The use of a dry-box and access to single crystals for Xray diffraction techniques made it possible to safely handle and characterize these complexes. The crystal structure of 2 shows that the five-coordinate ytterbium center is coordinated by a chelating diamido ligand, two thf molecules, and an iodine atom, forming a distorted square-pyramidal geometry. The N1, N2, O1, and O2 atoms form the basal plane, whilst the I1 occupies the apical position, as shown in Figure 1. The Yb1-N1, Yb1-N2, Yb1-O1, and Yb1-O2 bond lengths are 2.165(2), 2.179(2), 2.319(2), and 2.339(2) Å, respectively. The Yb1-I1 bond length is 2.9151 Å. However, the Yb<sup>II</sup>-N bond lengths of similar complex [(L<sup>Ph</sup>)Yb<sup>II</sup>(thf)<sub>3</sub>] in our previous work fall within the range 2.346(4)–2.394(4) Å.<sup>[18]</sup> The observed Yb<sup>III</sup>–N bond lengths of 2 are obviously shorter than the corresponding bond lengths of the ytterbium(II) complex, probably because of the smaller ionic radius of Yb<sup>III</sup> as compared to Yb<sup>II</sup>. As a result of the paramagnetic nature of 2, well-resolved NMR spectra could not be obtained for the trivalent ytterbium(III) complex.



bly influence the structure of the usually formed mononuclear or X-bridged dinuclear complexes " $[Cp_2Ln-(\mu-X)]_2$ ".<sup>[22]</sup> However, there is a growing interest in synthetic applications of  $\sigma$ -bonded organolanthanide complexes of composition R<sub>2</sub>LnX (Ln = Sm, Eu, Yb; X = Cl, Br, I).<sup>[23]</sup>

X-ray crystallographic results indicated that complex 3 contains two ytterbium(II) units bridged by a KI molecule, as shown in Figure 2. The L<sup>Ph</sup> ligands coordinate in a chelating fashion [Yb1-N1 2.322(6) Å, Yb1-N2 2.345(5) Å, Yb2–N3 2.346(6) Å, and Yb2–N4 2.323(6) Å], these Yb–N distances are apparently longer than those observed in related trivalent ytterbium species {e.g., five-coordinate  $[Yb(NHC_6H_3iPr_2-2,6)_3(thf)_2] = 2.17(2)-2.20(2) Å^{[12]}$  and complex 2}. The Yb–O (Et<sub>2</sub>O or thf) bond lengths are Yb1–O1 2.411(7) Å, Yb1–O2 2.375(7) Å, Yb2–O3 2.373(8) Å, and Yb2-O4 2.450(9) Å. The KI is just at the center of two ytterbium(II) groups with bond lengths Yb1-I1 3.235(1) Å, Yb2–I1 3.156(1) Å, and K1–I1 3.329(2) Å, and K···C bond lengths range from 2.957(7) to 3.484(10) Å. To the best of our knowledge, there are no previously reported examples of complexes containing a ytterbium(II) dimer assembled from cation- $\pi$  interactions.



Figure 1. Molecular structure of **2**. POV-RAY illustration, 30% thermal ellipsoids, all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1–N1 2.165(2), Yb1–N2 2.179(2), Yb1–O1 2.319(2), Yb1–O2 2.339(2), Yb1–I1 2.915(1), Si1–N1 1.722(2), Si1–N2 1.738(2); N1–Yb1–N2 72.65(8).

Bis(cyclopentadienyl) complexes of type "Cp<sub>2</sub>LnX", similar to complex **2**, have attracted increased attention, and derivatives of the latter are meanwhile established homogeneous catalysts.<sup>[21]</sup> Heteroligands X (e.g.,  $H^-$ ,  $X^-$ ) and the presence of neutral donor ligands (e.g., thf, OEt<sub>2</sub>) remarka-

Figure 2. Molecular structure of **3**, hydrogen atoms, Et<sub>2</sub>O, and thf molecules, omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1–N1 2.322(6), Yb1–N2 2.345(5), Yb2–N3 2.346(6), Yb2–N4 2.323(6), Yb1–O1 2.411(7), Yb1–O2 2.375(7), Yb2–O3 2.373(8), Yb2–O4 2.450(9), Yb1–Si1 2.997(2), Yb2–Si2 2.972(2), Yb1–I1 3.235(1), Yb2–I1 3.156(1), I1–K1 3.329(2); N1–Yb1–N2 68.36(19); N4–Yb2–N3 69.2(2).

The ligand  $[Ph_2Si(2,6-iPr_2C_6H_3N)_2]^{2-}$  (L<sup>Ph</sup>) seems an excellent candidate for the stabilization of divalent lanthanide complexes by means of cation- $\pi$  interactions.<sup>[18,19]</sup> Most



Cp-free divalent ytterbium complexes are mononuclear. Gambarotta et al. discovered an octameric macrocyclic structure consisting of eight [Ph<sub>2</sub>C(C<sub>4</sub>H<sub>3</sub>N)<sub>2</sub>Yb<sup>II</sup>] units with  $\sigma$  and  $\pi$  bonds and a flat tetrametallic unit with mixedvalent ytterbium.<sup>[24]</sup> A few years ago, a binuclear ytterbium(II) hydrido complex of a bulky hydrotris(pyrazolyl)borate ligand was reported.<sup>[25]</sup> Monoamide and guanidinate ligands with ytterbium(II) atoms were bridged by halogen atoms to form bimetallic complexes.<sup>[17,26]</sup> Therefore, the use of divalent lanthanide ions for the construction of oligomers is more difficult than the use of d-block metal analogues.<sup>[22,27]</sup> In complex **3**, the interaction between the alkali metal cation and the  $\pi$ -face of neutral aromatic system is an important binding force, which helps to stabilize the divalent ytterbium metal center. The construction of lanthanide–alkali chains,<sup>[28]</sup> layers,<sup>[29]</sup> and wheels<sup>[30]</sup> with  $\pi$ interactions has been a field of rapid growth, because of the formation of fascinating structures and their potential applications.<sup>[31]</sup>

## Conclusions

We have successfully synthesized the diamido complex of Yb<sup>II</sup> by the potassium reduction of a new Yb<sup>III</sup> starting material. This method proved to be efficient in the synthesis of some divalent ytterbium complexes in lanthanide chemistry. Our studies revealed that diamido ligand can be used as a ditopic linker to generate polymetallic complexes by taking advantage of the cation– $\pi$  interaction. The structural versatility and the novelty of these ytterbium complexes are a starting point for further investigations. The method might be extended to the synthesis of other lanthanide elements. The work is in progress in our laboratory.

Table 1. Crystal data and structure refinements for complexes 2 and 3.

## **Experimental Section**

**General Procedures:** All operations were performed under an inert atmosphere (<5 ppm oxygen or water) in a nitrogen-filled dry-box or by using standard Schlenk techniques. Solvents thf and *n*-hexane were freshly distilled from sodium benzophenone ketyl prior to use. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and were used as received unless otherwise indicated. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DPX300 spectrometer at 300.13 and 75.47 MHz, respectively.

#### Syntheses

**[(L<sup>Ph</sup>)Yb<sup>III</sup>I(thf)<sub>2</sub>] (2):** A solution of  $[Ph_2Si(2,6-iPr_2C_6H_3NH)_2]^{[20]}$ (0.77 g, 1.5 mmol) in thf (15 mL) was slowly added to a stirred suspension of KH (0.16 g, 4 mmol), and the resulting mixture was stirred for 2 h at room temperature. The yellow solution was then filtered to remove the excess of KH, and then a yellow solution of the potassium amido compound (1.5 mmol) in thf (15 mL) was treated with YbI<sub>3</sub> (0.83 g, 1.5 mmol) at room temperature for 4 h. The solvent was removed under reduced pressure, followed by addition of Et<sub>2</sub>O (40 mL). The Et<sub>2</sub>O extract of the solid was filtered, reduced to approximately 5 mL, and kept for several days at room temperature, after which single crystals of **2** suitable for X-ray crystallographic studies were obtained to give the title compound **2** as red crystals (69%). C<sub>44</sub>H<sub>60</sub>IN<sub>2</sub>O<sub>2</sub>SiYb (977.00): calcd. C 54.09, H 6.19, N 2.87; found C 53.78, H 5.94, N 2.49.

**[{(L<sup>Ph</sup>)Yb<sup>II</sup>(thf)(Et<sub>2</sub>O)}<sub>2</sub>(μ-KI)] (3).** A thf solution of complex **2**  $[(L^{Ph})YbI(thf)_2]$  (1.01 g, 1.0 mmol) was stirred with an excess of K (0.06 g, 1.5 mmol) for 6 h at room temperature. The solvent was removed under reduced pressure, followed by addition of Et<sub>2</sub>O (40 mL). The Et<sub>2</sub>O extract of the solid was filtered, reduced to approximately 3 mL, and kept for several days at room temperature, after which single crystals of **3** suitable for X-ray crystallographic studies were obtained to give the title compound **3** as deep red crystals (39%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta$  = 7.82 (d, *J* = 4.8 Hz, 4 H, Ar*H*), 7.24–7.05 (m, 10 H, Ar*H*), 6.99 (t, *J* = 7.2 Hz, 2 H, Ar*H*), 3.26–3.54 (m, 8 H, *thf*), 4.33 (sept., *J* = 6.9 Hz, 4 H,

Empirical formula	C <sub>44</sub> H <sub>60</sub> IN <sub>2</sub> O <sub>2</sub> SiYb	$C_{88}H_{124}IKN_4O_4Si_2Yb_2$
Formula weight	976.97	1870.17
Temperature [K]	173(2)	173(2)
Crystal system	orthorhombic	orthorhombic
Space group	Pbca	Pbca
a [Å]	19.9934(6)	23.6218(9)
b [Å]	18.4582(5)	21.3970(7)
c [Å]	23.4780(7)	34.5017(12)
Volume [Å <sup>3</sup> ]	8664.4(4)	17438.4(11)
Z	8	8
Density (calculated) [Mgm <sup>-3</sup> ]	1.498	1.425
Absorption coefficient [mm <sup>-1</sup> ]	2.935	2.610
F(000)	3928	7616
Crystal size [mm]	$0.30 \times 0.20 \times 0.20$	$0.28 \times 0.23 \times 0.19$
$\theta$ range for data collection	1.73 to 26.07°	1.18 to 26.04°
Reflection collected	46356	94252
Independent reflections	8572 [R(int) = 0.0304]	17202 [R(int) = 0.0619]
Completeness to $\theta$	$\theta = 26.07^{\circ}, 100.0\%$	$\theta = 26.04^{\circ}, 100.0\%$
Max. and min. transmission	0.5914 and 0.4730	0.6369 and 0.5285
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	8572/0/460	17202/47/827
Goodness-of-fit on $F^2$	1.044	1.037
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0235, wR2 = 0.0565	R1 = 0.0582, wR2 = 0.1341
R indices (all data)	R1 = 0.0330, wR2 = 0.0616	R1 = 0.0995, wR2 = 0.1869
Largest diff. peak and hole [ eÅ <sup>-3</sup> ]	0.733 and -0.496	2.360 and -2.307

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CHMe<sub>2</sub>), 1.25–1.44 (br., 8 H, *thf*), 1.11 (d, J = 6.9 Hz, 24 H, CHMe<sub>2</sub>) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75.47 MHz):  $\delta = 161.3$ , 158.2, 149.4, 143.4, 135.8, 126.8, 124.9, 116.4, 69.1, 28.2 [OCH<sub>2</sub>CH<sub>2</sub>(thf)], 25.7, 23.9 (CHMe<sub>2</sub>) ppm. C<sub>80</sub>H<sub>104</sub>IKN<sub>4</sub>O<sub>2</sub>Si<sub>2</sub>Yb<sub>2</sub> (1722.0) (**3** – 2OEt<sub>2</sub>): calcd. C 55.80, H 6.09, N 3.25; found C 55.59, H 6.14, N 2.99.

**X-ray Structure Determination:** All single crystals were immersed in Paratone-N oil and sealed under N<sub>2</sub> in thin-walled glass capillaries. Data were collected at 173 K with a Bruker SMART II CCD diffractometer by using Mo- $K_a$  radiation. An empirical absorption correction was applied with the SADABS program.<sup>[32]</sup> All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on  $F^2$  by using the SHELXTL program package.<sup>[33]</sup> Most of the carbon hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed by using the riding model. Crystal data and details of data collection and structure refinements are given in Table 1.

CCDC-722477 and -722478 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.

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