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# Deprotonation of β-Diketiminate in Sterically Demanding β-(Diketiminato)lanthanide Complexes: Influence of Lanthanide Metals

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Attempted synthesis of tris(β-diketiminato)lanthanide complexes [Ln($\mathbf{L}^{2,6\text{-Me}_2}$)$_3$] ($\mathbf{L}^{2,6\text{-Me}_2}$ = [{N(C$_6$H$_3$Me$_2$-2,6)C(Me)}$_2$CH]) resulted in ligand deprotonation, and different outcomes depending on the central metal used were observed. Reaction of YbCl$_3$ with Na$\mathbf{L}^{2,6\text{-Me}_2}$ (3 equiv.) afforded the five-membered cyclometalated ytterbium β-diketiminate complex [Yb($\mathbf{L}^{2,6\text{-Me}_2}$)($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}}$] (**1**). The same reaction with LnCl$_3$ (Ln = Nd, Sm, and Er) gave the new complexes composed of one normal $\mathbf{L}^{2,6\text{-Me}_2}$ and one deprotonated neighboring benzazacyclopentane ligand derived from deprotonation of the 2-methyl group followed by an attack of the carbon atom on the β-diketiminate backbone, [Ln($\mathbf{L}^{2,6\text{-Me}_2}$)($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}'}$(thf)] [Ln = Nd (**2**), Sm (**3**), and Er (**4**)]. The bonding mode in the {Ln($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}'}$} moiety was also found to depend on the central metal ions.

## Introduction

Bidentate β-diketiminate monoanions have been widely used as spectator ligands in coordination chemistry and organometallic chemistry of lanthanide metals.[1] These ligands have also been proven under certain conditions to undergo transformations that include reduction to di- or trianionic species by a reducing agent,[2] deprotonation to a dianion by means of an alkane elimination[3a–e] or a β-diketiminate elimination,[3f] and oxidation coupling to a neutral molecule.[4] Recently we have reported that the β-diketiminate group in a sterically demanding complex, such as tris(β-diketiminato)lanthanide complex, can also serve as an active species in homogeneous catalysis, and the activity was found to depend both on the size of the β-diketiminato ligands and the central metals.[5] These results encouraged us to synthesize tris(β-diketiminato)lanthanide complexes with a bulky ligand $\mathbf{L}^{2,6\text{-Me}_2}$ ($\mathbf{L}^{2,6\text{-Me}_2}$ = [{N(C$_6$H$_3$Me$_2$-2,6)C(Me)}$_2$CH]) in an attempt to extend the synthesis and reactive chemistry of tris(β-diketiminato)lanthanide complexes. The metathesis reactions of Na$\mathbf{L}^{2,6\text{-Me}_2}$ with various LnCl$_3$ from early to late lanthanide metals (Nd, Sm, Er, and Yb) were conducted in a molar ratio of 3 to 1 with the aim of understanding the influence of the size of the metals. However, no matter whether the metal was large (Nd) or small (Yb), none of the metathesis reactions afforded the target complexes [Ln($\mathbf{L}^{2,6\text{-Me}_2}$)$_3$], but rather new complexes that contained one "normal" ligand and one deprotonated ligand by a β-diketiminato ligand elimination. Moreover, we observed different outcomes depending on the central metal ions used: a cyclometalated complex [Yb($\mathbf{L}^{2,6\text{-Me}_2}$)($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}}$] for Yb and the complexes with a neighboring benzazacyclopentane ligand [Ln($\mathbf{L}^{2,6\text{-Me}_2}$)($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}'}$(thf)] for Nd, Sm, and Er. Here we report the results.

## Results and Discussion

### Synthesis and Molecular Structure of Cyclometalated Ytterbium(III) Complex [Yb($\mathbf{L}^{2,6\text{-Me}_2}$)($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}}$] (1)

The tris(β-diketiminato)ytterbium complex with the β-diketiminato ligand bearing one methyl group at the 2-position on the phenyl ring, [Yb($\mathbf{L}^{2\text{-Me}}$)$_3$] ($\mathbf{L}^{2\text{-Me}}$ = [{N(C$_6$H$_4$Me-2)C(Me)}$_2$CH]), has recently been found to be stable.[5b] Thus, the reaction of YbCl$_3$ with a more bulky β-diketiminate sodium salt Na$\mathbf{L}^{2,6\text{-Me}_2}$ was tested in THF to see whether [Yb($\mathbf{L}^{2,6\text{-Me}_2}$)$_3$] could also be prepared. The reaction proceeded well at 60 °C and gave the dark green solution from which dark green crystals were obtained in 41% yield upon crystallization at room temperature. However, elemental analysis and single-crystal X-ray diffraction determination demonstrated that the crystals were not the expected [Yb($\mathbf{L}^{2,6\text{-Me}_2}$)$_3$], but the cyclometalated ytterbium(III) complex [Yb($\mathbf{L}^{2,6\text{-Me}_2}$)($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}}$] (**1**) instead. Complex **1** contains both the monoanionic ligand $\mathbf{L}^{2,6\text{-Me}_2}$ and its deprotonation partner ($\mathbf{L}^{2,6\text{-Me}_2}$)$^{\text{dep}}$ by the elimination of one β-diketiminato ligand (Scheme 1).

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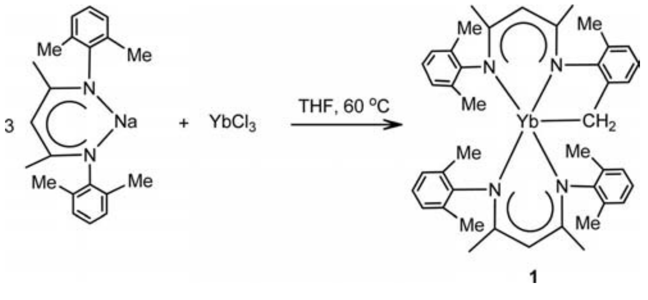
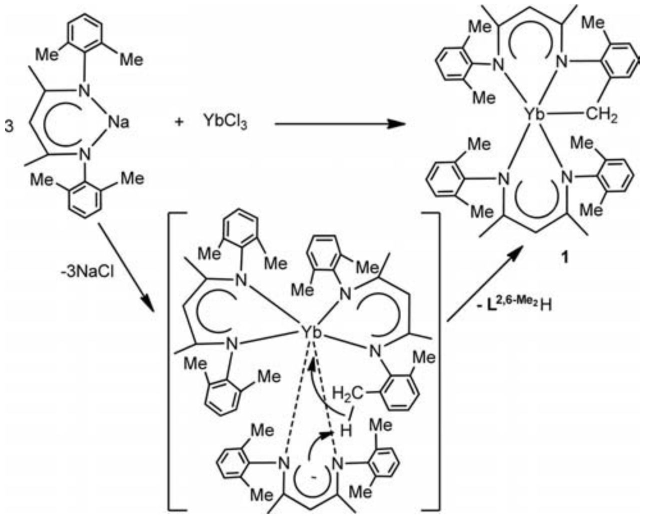


Scheme 1.

Further experiments indicated that a monochloride derivative [Yb(**L**$^{2,6\text{-Me}_2}$)$_2$Cl] could be isolated when $YbCl_3$ was treated with Na**L**$^{2,6\text{-Me}_2}$ in a molar ratio of 1 to 2. These results demonstrated that the synthesis of tris(β-diketiminato)lanthanide complexes is very sensitive to the size of the β-diketiminato ligand. Addition of the second methyl group at the 6-position on a phenyl ring led to an **L**$^{2,6\text{-Me}_2}$ ligand that was too bulky to stabilize the tris(β-diketiminato)ytterbium complex.

The self-deprotonation reaction of the β-diketiminato ligand was first reported in the case of the reaction of [Pb(**L**′)$_2$] with [Yb(**L**′)$_2$] (**L**′ = [{N(SiMe$_3$)C(Ph)}$_2$CH]). The reaction led to a four-membered cyclometalated ytterbium(III) β-diketiminate complex, [Yb(**L**′)(**L**′)$^{\text{dep}}$].[3f] In our case, the five-membered cyclometalated ytterbium was formed because of the presence of an *ortho*-methyl group at the phenyl ring. According to the pathway suggested for the synthesis of [Yb(**L**′)(**L**′)$^{\text{dep}}$],[3f] complex **1** may be formed through an unstable intermediate [{Yb(**L**$^{2,6\text{-Me}_2}$)$_2$}(**L**$^{2,6\text{-Me}_2}$)] as shown in Scheme 2.



Scheme 2.

The reaction first afforded an unstable transient intermediate [{Yb(**L**$^{2,6\text{-Me}_2}$)$_2$}(**L**$^{2,6\text{-Me}_2}$)]. On account of the overcrowded coordination environment around the central Yb metal by three β-diketiminato ligands, the third loosely attached ligand **L**$^{2,6\text{-Me}_2}$ deprotonated one of the methyl groups activated by a Yb···Me agostic interaction. An attempt to isolate the intermediate [{Yb(**L**$^{2,6\text{-Me}_2}$)$_2$}(**L**$^{2,6\text{-Me}_2}$)] was unsuccessful.

The molecular structure of **1** is illustrated in Figure 1. The selected bond lengths and angles are listed in Table 1. The central Yb ion bonded to N1 and N2 from a monoanionic **L**$^{2,6\text{-Me}_2}$, thereby forming a boat-shaped β-diketiminate ytterbium moiety, and to the bicyclic ligand through N3, N4, and C41. The bonding mode in the {Yb(**L**$^{2,6\text{-Me}_2}$)} part is close to $\eta^5$, which is similar to that in reported [Yb(**L**′)(**L**′)$^{\text{dep}}$],[3f] and the bond parameters in {Yb(**L**$^{2,6\text{-Me}_2}$)} are comparable with the corresponding data in $\eta^5$-bonded complexes of [Yb(**L**′)(**L**′)$^{\text{dep}}$][3f] and [Yb{N(SiMe$_3$)C(C$_6$H$_4$Me-4)C(H)C(adamantyl-1)N(SiMe$_3$)}$_2$].[6] In the {Yb(**L**$^{2,6\text{-Me}_2}$)$^{\text{dep}}$} part, the Yb atom is coordinated by the novel bianionic ligand [(**L**$^{2,6\text{-Me}_2}$)$^{\text{dep}}$]$^{2-}$ through two nitrogen atoms (N3 and N4) and one carbon atom (C41). The Yb–C41 bond length of 2.380(3) Å is 0.026 Å shorter than 2.406 Å in [Yb(**L**′)(**L**′)$^{\text{dep}}$],[3f] which may be due to the requirement of weak interactions between the two aromatic carbon atoms (C35 and C36), respectively, to Yb. The Yb–N4 bond length of 2.291(3) Å is consistent with 2.289(2) Å in [Yb(**L**′)(**L**′)$^{\text{dep}}$].[3f] The distances of Yb···C35 [2.858(3) Å] and Yb···C36 [2.788(3) Å] are in the range observed in the other known complexes of lanthanide π-arene interactions.[7]

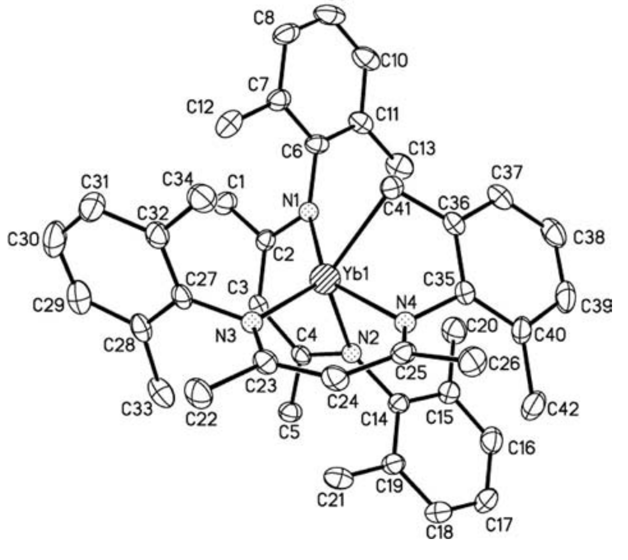


Figure 1. ORTEP diagram of **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

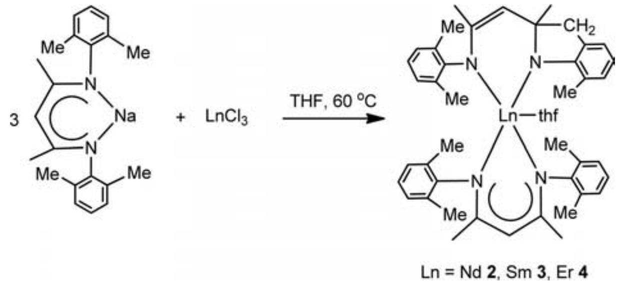
### Syntheses and Molecular Structures of [Ln(L$^{2,6\text{-Me}_2}$)(L$^{2,6\text{-Me}_2}$)$^{\text{dep}'}$(thf)] [Ln = Nd (2), Sm (3), and Er (4)]

The same reaction with a large metal chloride, $NdCl_3$, was then tried to address the influence of the size of metal. Treatment of $NdCl_3$ with Na**L**$^{2,6\text{-Me}_2}$ (3 equiv.) at 60 °C gave the yellow-green crystals from a mixture of THF and hexane. The full characterization of the crystals, including X-

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

| Yb1–N1 | 2.297(3) | Yb1–N2 | 2.283(3) | Yb1–N3 | 2.286(3) |
|---|---|---|---|---|---|
| Yb1–N4 | 2.291(3) | Yb1–C2 | 2.962(3) | Yb1–C3 | 3.048(4) |
| Yb1–C4 | 2.951(3) | Yb1–C35 | 2.858(3) | Yb1–C36 | 2.788(3) |
| Yb1–C41 | 2.380(3) | N1–C2 | 1.328(4) | N2–C4 | 1.333(4) |
| N3–C23 | 1.354(4) | N4–C35 | 1.435(4) | C2–C3 | 1.409(5) |
| C3–C4 | 1.405(5) | C23–C24 | 1.379(5) | C24–C25 | 1.419(5) |
| C35–C36 | 1.418(5) | C36–C41 | 1.462(5) | | |
| N1–Yb1–N2 | 84.51(10) | N1–Yb1–N3 | 133.00(10) | N1–Yb1–N4 | 146.08(9) |
| N2–Yb1–N3 | 113.72(10) | N2–Yb1–N4 | 93.46(10) | N3–Yb1–N4 | 78.58(10) |
| N4–Yb1–C41 | 69.88(11) | C35–N4–Yb1 | 97.47(19) | C36–C41–Yb1 | 89.8(2) |
| C36–C35–N4 | 112.5(3) | C35–C36–C41 | 118.7(3) | | |

ray crystal structure determination, revealed the crystals to be a deprotonated complex, $[\mathrm{Nd}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})^{\mathrm{dep}'}(\mathrm{thf})]$ (**2**), not the $[\mathrm{Nd}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})_3]$ complex. The occurrence of the deprotonation reaction here indicates that even with a large metal (Nd), the ligand $\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ is still too big to form stable $[\mathrm{Nd}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})_3]$. Complex **2** has a new structural skeleton that contains one normal $\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ and one neighboring benzazacyclopentane ligand derived from deprotonation of the 2-methyl group followed by an attack of the carbon atom on the β-diketiminate backbone as shown in Scheme 3.



Scheme 3.

The formation of a new Nd complex **2** prompted us to further study the reactions with other lanthanide metal chlorides. Thus, reactions of $\mathrm{Na}\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ with middle and later metal chlorides, $SmCl_3$ and $ErCl_3$, were conducted in THF at 60 °C. Red and dark-brown crystals, respectively, were isolated in good yields. Both crystals were characterized by X-ray diffraction to be the corresponding complexes $[\mathrm{Sm}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})^{\mathrm{dep}'}(\mathrm{thf})]$ (**3**) and $[\mathrm{Er}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})^{\mathrm{dep}'}(\mathrm{thf})]$ (**4**), which are analogues of complex **2** (Scheme 3). The formation of **2**–**4** may be attributed to the absence of an Ln···Me agostic interaction in their intermediates.

Complexes **2**–**4** are sensitive to air and moisture but thermostable. They decomposed at 127–129, 123–124, and 90–93 °C, respectively.

Complexes **2**–**4** all contain a coordinated thf molecule. Their molecular structures are shown in Figure 2. The selected bond lengths and angles are listed in Table 2. The central metal in each complex is coordinated by one monoanionic β-diketiminato ligand $\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ in a chelating mode through two nitrogen atoms (N1 and N2), one dianionic neighboring benzazacyclopentane ligand, and one thf molecule. The bond parameters in the $\{\mathrm{Ln}\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}\}$ part of each complex are highly comparable to those found in the corresponding $[\mathrm{Ln}(\mathbf{L}^{4\text{-}\mathrm{Me}})_3]$.[5]

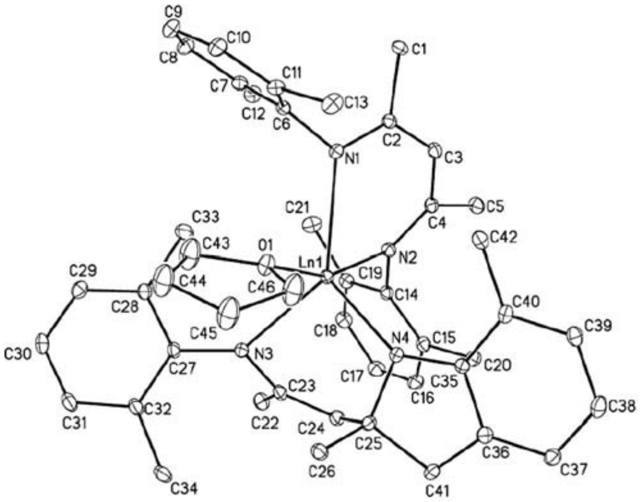


Figure 2. ORTEP diagram of $[\mathrm{Ln}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})^{\mathrm{dep}'}(\mathrm{thf})]$ [Ln = Nd (**2**), Sm (**3**), Er (**4**)] showing the atom-numbering scheme thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

However, differences in bonding mode in the $\{\mathrm{Ln}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})^{\mathrm{dep}'}\}$ part were observed among them. In complexes **2** and **3**, the novel ligand can be best described as implicating $\eta^3$-1-azaallyl (N3–C23–C24) and amide (N4) bonds to the metals. The distances of Ln···C23 and Ln···C24 are 2.859(7) and 3.001(7) Å for Nd, and 2.932(9) and 3.110(9) Å for Sm, respectively, which are in the range of intramolecular π-arene···Ln interactions. In complex **2**, a weak interaction between Nd and C25 was also observed because the distance of Nd···C25 is 3.093(7) Å; subtraction of an extrapolated radius (0.983 Å) for six-coordinate $Nd^{3+}$ from Nd···C gives 2.11 Å, well within the upper limit (2.16 Å) for significant intramolecular π-arene···Ln interactions.[8] The distance of Sm···C25 is longer than the upper value of π-arene···Ln bonding.

In complex **4**, the $\{\mathrm{Er}(\mathbf{L}^{2,6\text{-}\mathrm{Me}_2})^{\mathrm{dep}'}\}$ moiety can be best described as $\eta^2$-1,5 diazapentene-2 (N3, N4) bonds to the metal. The distance of Er···C23 is 2.965(6) Å, thus indicating the presence of a C23···Er interaction. But the distance of Er···C24 [3.171(6) Å] is far from the limit value for a

Table 2. Selected bond lengths [Å] and bond angles [°] for complexes **2**–**4**.

| | **2** | **3** | **4** | | **2** | **3** | **4** |
|---|---|---|---|---|---|---|---|
| Ln1–N1 | 2.471(8) | 2.536(6) | 2.392(4) | Ln1–N2 | 2.487(6) | 2.489(6) | 2.394(4) |
| Ln1–N3 | 2.293(8) | 2.349(6) | 2.215(5) | Ln1–N4 | 2.231(7) | 2.291(6) | 2.180(4) |
| Ln1–O1 | 2.526(5) | 2.581(5) | 2.426(3) | Ln1–C23 | 2.932(9) | 2.859(7) | 2.965(6) |
| Ln1–C24 | 3.110(9) | 3.001(7) | 3.171(6) | N1–C2 | 1.339(12) | 1.333(9) | 1.350(7) |
| N2–C4 | 1.342(10) | 1.328(9) | 1.339(7) | N3–C23 | 1.376(11) | 1.407(9) | 1.413(7) |
| N4–C25 | 1.499(13) | 1.504(9) | 1.516(8) | N4–C35 | 1.402(13) | 1.394(9) | 1.396(7) |
| C2–C3 | 1.387(13) | 1.397(10) | 1.390(8) | C3–C4 | 1.396(13) | 1.415(10) | 1.396(8) |
| C23–C24 | 1.363(14) | 1.363(10) | 1.334(8) | C24–C25 | 1.530(16) | 1.518(10) | 1.524(8) |
| C25–C41 | 1.526(14) | 1.571(10) | 1.542(8) | C35–C36 | 1.431(14) | 1.404(10) | 1.423(9) |
| C36–C41 | 1.512(18) | 1.496(11) | 1.501(10) | | | | |
| N1–Ln1–N2 | 76.6(2) | 75.27(18) | 79.26(15) | N3–Ln1–N2 | 96.6(2) | 113.8(2) | 97.69(15) |
| N4–Ln1–N3 | 97.6(3) | 95.4(2) | 98.43(19) | N4–Ln1–N1 | 124.0(3) | 127.94(19) | 124.57(17) |
| N3–Ln1–N1 | 138.3(3) | 134.45(19) | 136.84(16) | N4–Ln1–N2 | 99.1(2) | 100.8(2) | 100.96(15) |
| N4–Ln1–O1 | 92.9(2) | 85.98(18) | 90.59(14) | N3–Ln1–O1 | 93.0(2) | 82.97(19) | 90.78(15) |
| N1–Ln1–O1 | 87.2(2) | 86.37(18) | 85.65(14) | N2–Ln1–O1 | 163.4(2) | 160.82(19) | 164.46(15) |
| N4–C25–C41 | 104.4(10) | 109.2(6) | 107.1(5) | C35–N4–C25 | 107.0(8) | | |
| C36–C41–C25 | 103.3(9) | | | N4–C35–C36 | 111.3(11) | | |
| C35–C36–C41 | 107.1(9) | | | | | | |

weak π-arene···Ln interaction. The differences in bonding mode observed among the three complexes may be attributed to the differences in the amount of steric hindrance around the central metals that results from the size of metals: the smallest ionic radius of Er leads to the most crowded coordinated sphere. The bond lengths of C25–C41 in **2**–**4** are highly comparable to each other and are consistent with the value of a C–C single bond.

## Conclusion

The reaction of $\mathrm{LnCl_3}$ (Ln = Nd, Sm, Er, and Yb) with $\mathrm{Na}\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ (3 equiv.) leads to the sterically induced self-deprotonation of $\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ with the formation of novel complexes **1**–**4**. The structural motif of **1**–**4** depends on the lanthanide metals: the cyclometalated β-diketiminate complex for the smallest metal Yb, and the complexes [Ln($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)$^{\mathrm{dep}'}$(thf)] with a neighboring benzazacyclopentane partner for Nd, Sm, and Er. Moreover, the influence of lanthanide metals on the bonding mode in the {Ln($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)$^{\mathrm{dep}'}$} moiety for complexes **2**–**4** was also observed. Further study of the reactivity of β-diketiminate in sterically demanding lanthanide complexes continues in our laboratory.

## Experimental Section

**General Procedures:** All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl before use. $\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$H was prepared according to the literature method.[9] Anhydrous $\mathrm{LnCl_3}$ was prepared according to the literature procedure.[10] Lanthanide analyses were performed by ethylenediaminetetraacetic acid (EDTA) titration with a xylenol orange indicator and a hexamine buffer.[11] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion using a Carlo–Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. The uncorrected melting points of crystalline samples were determined in sealed Ar-filled capillaries.

**[Yb($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)$^{\mathrm{dep}}$] (1):** The solution of $\mathrm{Na}\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ in THF (15.7 mL, 8.70 mmol) that was formed by the reaction of NaH with $\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$H in THF at room temperature was added to a slurry of anhydrous $\mathrm{YbCl_3}$ (0.81 g, 2.90 mmol) in THF (about 10 mL). The reaction mixture was stirred at 60 °C for 24 h. The undissolved portion was removed by centrifugation and the dark green solution was concentrated to about 1 mL. Hexane (5 mL) was then added. The solution was cooled to –10 °C for crystallization to give dark green crystals in 41% (0.96 g) yield; m.p. 72–75 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3046 (w), 3019 (w), 2916 (m), 2853 (w), 1659 (m), 1624 (s), 1553 (s), 1468 (s), 1379 (m), 1277 (m), 1182 (m), 1092 (m), 1028 (w), 988 (w), 918 (w), 766 (s), 694 (w), 596 (w), 569 (w), 520 (w), 484 (w), 440 (w) $\mathrm{cm^{-1}}$. $\mathrm{C_{42}H_{49}N_4Yb}$ (782.89): calcd. C 64.43, H 6.31, N 7.16, Yb 22.10; found C 63.63, H 6.67, N 6.71, Yb 21.96.

**[Nd($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)$^{\mathrm{dep}'}$(thf)] (2):** Complex **2** was prepared by the same procedure as that for complex **1**, but anhydrous $\mathrm{NdCl_3}$ (0.72 g, 2.87 mmol) in THF (about 10 mL) and the solution of $\mathrm{Na}\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ (28.2 mL, 8.61 mmol) in THF were used. The yellow-green crystals of complex **2** from a mixture of THF (1 mL) and hexane (4 mL) were isolated at 5 °C in 71% (1.68 g) yield; m.p. 127–129 °C. IR (KBr): $\tilde{\nu}$ = 3017 (s), 2963 (s), 2918 (s), 2855 (s), 1653 (s), 1624 (s), 1597 (s), 1552 (s), 1466 (s), 1379 (s), 1273 (s), 1091 (m), 1026 (m), 984 (w), 921 (w), 764 (s), 631 (w), 526 (w), 448 (w) $\mathrm{cm^{-1}}$. $\mathrm{C_{46}H_{57}N_4NdO}$ (826.20): calcd. C 66.87, H 6.95, N 6.78, Nd 17.46; found C 66.22, H 6.86, N 6.76, Nd 16.99.

**[Sm($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)($\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$)$^{\mathrm{dep}'}$(thf)] (3):** By the same procedure as that for complex **2**, red crystals of complex **3** were obtained from the treatment of $\mathrm{SmCl_3}$ (1.30 g, 5.06 mmol) with $\mathrm{Na}\mathbf{L}^{2,6\text{-}\mathrm{Me}_2}$ (25.8 mL, 15.18 mmol) upon crystallization from a mixture of (about 1 mL) and hexane (4 mL) at 5 °C; yield 1.90 g, 45%; m.p. 123–124 °C. IR (KBr): $\tilde{\nu}$ = 2963 (w), 2912 (w), 2851 (w), 1660 (m), 1624 (s), 1553 (s), 1469 (m), 1373 (m), 1276 (m), 1091 (m), 1026 (w), 997 (w), 804 (w), 765 (s), 631 (m), 517 (m), 448 (w) $\mathrm{cm^{-1}}$. $\mathrm{C_{46}H_{57}N_4OSm}$

Table 3. Crystallographic data for complexes **1**–**4**.

| | **1** | **2**·$C_4H_8O$ | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{42}H_{49}N_4Yb$ | $C_{50}H_{65}N_4O_2Nd$ | $C_{46}H_{57}N_4OSm$ | $C_{46}H_{57}N_4OEr$ |
| Formula weight | 782.89 | 898.30 | 832.31 | 849.22 |
| $T$ [K] | 223(2) | 223(2) | 293(2) | 223(2) |
| Crystal system | monoclinic | monoclinic | orthorhombic | orthorhombic |
| Space group | $P21/n$ | $C2/c$ | $Pbcn$ | $Pbcn$ |
| Crystal size [mm$^3$] | 0.70 × 0.50 × 0.40 | 0.60 × 0.12 × 0.10 | 0.60 × 0.58 × 0.30 | 0.30 × 0.30 × 0.20 |
| $a$ [Å] | 11.7812(9) | 28.705(2) | 18.2397(15) | 18.0005(10) |
| $b$ [Å] | 14.8560(11) | 20.7724(12) | 11.6238(9) | 11.4813(8) |
| $c$ [Å] | 20.9300(16) | 20.8219(17) | 38.654(4) | 38.644(2) |
| $\beta$ [°] | 93.581(2) | 132.4560(10) | 90 | 90 |
| $V$ [Å$^3$] | 3656.0(5) | 9160.0(12) | 8195.3(12) | 7986.5(9) |
| $Z$ | 4 | 8 | 8 | 8 |
| $D_{\text{calcd.}}$ [mg cm$^{-3}$] | 1.422 | 1.303 | 1.349 | 1.413 |
| $\mu$ [mm$^{-1}$] | 2.592 | 1.175 | 1.472 | 2.141 |
| $F$ (000) | 1596 | 3752 | 3448 | 3496 |
| $\theta$ range [°] | 3.02–25.50 | 3.05–25.50 | 3.03–25.35 | 3.06–25.50 |
| Reflections collected/unique | 18377/6776 | 23456/8515 | 54769/7324 | 21992/7350 |
| $R$(int) | 0.0274 | 0.0581 | 0.0736] | [0.0437 |
| Data/restraints/parameters | 6776/0/436 | 8515/12/487 | 7324/1/421 | 7350/1/481 |
| Goodness-of-fit on $F^2$ | 1.116 | 1.130 | 1.178 | 1.165 |
| final $R$ [$I > 2\sigma(I)$] | 0.0287 | 0.0737 | 0.0858 | 0.0515 |
| $wR_2$ (all data) | 0.0629 | 0.1701 | 0.2187 | 0.0948 |

(832.31): calcd. C 66.38, H 6.90, N 6.73, Sm 18.06; found C 66.85, H 6.92, N 6.73, Sm 17.90.

**[Er($L^{2,6\text{-}Me_2}$)($L^{2,6\text{-}Me_2}$)$^{dep'}$(thf)] (4):** By the same procedure as that for complex **2**, the dark brown crystals of complex **4** were obtained from the treatment of $ErCl_3$ (0.46 g, 1.68 mmol) with Na$L^{2,6\text{-}Me_2}$ (16.5 mL, 5.04 mmol) upon crystallization from a mixture of THF (about 1 mL) and hexane (4 mL) at 15 °C; yield 0.57 g, 40 %; m.p. 90–93 °C. IR (KBr): $\tilde{\nu}$ = 3018 (w), 2963 (m), 2916 (m), 2855 (w), 1659 (s), 1624 (s), 1597 (s), 1553 (s), 1468 (s), 1369 (s), 1279 (m), 1184 (m), 1092 (m), 1032 (w), 766 (s), 635 (w), 519 (w), 421 (m) cm$^{-1}$. $C_{46}H_{57}ErN_4O$ (849.22): calcd. C 65.06, H 6.77, N 6.60, Er 19.72; found C 64.52, H 6.69, N 6.73, Er 19.33.

**X-ray Crystallography:** Suitable single crystals of complexes **1**–**4** were sealed in a thin-walled glass capillary, respectively, for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in $\omega$ scan mode by using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71070 Å). 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 3.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C–H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined by using SHELEXL-97 program.

CCDC-783856 (for **1**), -783857 (for **2**), -783858 (for **3**), and -783859 (for **4**) 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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