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PAPER

Reduction of Sterically Hindered β-Diketiminato Europium(III) Complexes by the β-Diketiminato Anion: A Convenient Route for the Synthesis of β-Diketiminato Europium(II) Complexes†

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The metathesis reaction of anhydrous $EuCl_3$ with sodium salt of bulky β-diketiminato NaL (L = $[N(2,4,6\text{-}Me_3C_6H_2)C(Me)]_2CH^-$, $L^{2,4,6\text{-Me3}}$; $[N(2,6\text{-}{}^iPr_2C_6H_3)C(Me)]_2CH^-$, $L^{2,6\text{-ipr2}}$ and $[(2,6\text{-}{}^iPr_2C_6H_3)NC(Me)CHC(Me)N(C_6H_5)]^-$, $L^{2,6\text{-ipr2}}{}_{Ph}$) in THF at 60 °C afforded the corresponding Eu^{II} complexes: $Eu^{II}(L^{2,4,6\text{-Me3}})_2(THF)$ (**1**), $Eu^{II}(L^{2,6\text{-ipr2}})_2$ (**2**) and $Eu^{II}(L^{2,6\text{-ipr2}}{}_{Ph})_2$ (**5**) with the formations of dimers $(L^{2,4,6\text{-Me3}})_2$ (**3**) and $(L^{2,6\text{-ipr2}})_2$ (**4**) for the former two reactions and proligand $L^{2,6\text{-ipr2}}{}_{Ph}H$ (**6**) for the latter one. Compounds **1–6** were confirmed by an X-ray crystal structure analysis. The central metal Eu^{II} in **1** is coordinated by two monoanionic $L^{2,4,6\text{-Me3}}$ ligands and one THF molecule in a trigonal bipyramid. The Eu^{II} in each of **2** and **5** is ligated by two monoanionic ligands to form a tetrahedral geometry. The BVS (Bond Valence Sum) calculation indicates the oxidation state of Eu in all the three complexes is 2+ (2.12 for **1**, 1.86 for **2** and 1.99 for **5**). The isolation of dimers of $(L^{2,4,6\text{-Me3}})_2$ and $L^{2,6\text{-ipr2}})_2$ and proligand $L^{2,6\text{-ipr2}}{}_{Ph}H$ demonstrates that the reducing agent in the present reduction of a Eu^{III} ion to a Eu^{II} ion might be the $(L^{2,4,6\text{-Me3}})^-$, $(L^{2,6\text{-ipr2}})^-$ and $(L^{2,6\text{-ipr2}}{}_{Ph})^-$, respectively. The possible mechanism for the reduction pathway is presented.

Introduction

The application of β-diketiminates as monoanionic ancillary ligands has attracted increasing attention in organometallic chemistry of lanthanide metals because their electronic and steric factors can be tuned by variation of the substituents on the nitrogen atoms or at their skeleton.[1] However, recent results revealed that β-diketiminato ligands themselves can participate in transformations under certain conditions, including reduction by the addition of a strong reducing agent,[2] or an external strong base,[3] and self-deprotonation by the elimination of a β-diketiminato ligand induced from steric demand in a sterically hindered lanthanide(III) complex.[1f,1l]

Very recently, we have found that the β-diketiminato ligand in a sterically crowded tris(β-diketiminato) lanthanide complex could serve as either an active species to catalyze ring opening polymerization of lactones and addition of amines to carbodiimides with high activity,[1i,1k] or an efficient reducing agent in the case of Eu metal to reduce an Eu(III) ion to an Eu(II) ion by giving up an electron to Eu(III) ion. Thus, the divalent Eu complex $Eu^{II}(L^{2,6\text{-Me2}})_2(THF)$ ($L^{2,6\text{-Me2}}$ = $[N(2,6\text{-}Me_2C_6H_3)C\text{-}(Me)]_2CH^-$) and the dimer $(L^{2,6\text{-Me2}})_2$ were isolated from the reaction of $EuCl_3$ with three equivalents of $NaL^{2,6\text{-Me2}}$.[2]

To assess the generality of reduction reaction of Eu(III) by β-diketiminato anions in sterically hindered β-diketiminato Eu^{III} complexes, we continue to study the metathesis reaction of $EuCl_3$ with the sodium salts of the following three β-diketiminato ligands: two symmetrical β-diketiminato ligands $L^{2,4,6\text{-Me3}}H$ ($L^{2,4,6\text{-Me3}}$ = $[N(2,4,6\text{-}Me_3C_6H_2)C(Me)]_2CH^-$) and $L^{2,6\text{-ipr2}}H$ ($L^{2,6\text{-ipr2}}$ = $[N(2,6\text{-}{}^iPr_2C_6H_3)C(Me)]_2CH^-$) and one asymmetrical β-diketiminato ligand $L^{2,6\text{-ipr2}}{}_{Ph}H$ ($L^{2,6\text{-ipr2}}{}_{Ph}$ = $[(2,6\text{-}{}^iPr_2C_6H_3)\text{-}NC(Me)CHC(Me)N(C_6H_5)]^-$). Indeed, each reaction afforded a Eu(II) complex plus either a dimer of a ligand (for the reaction with the symmetrical ligand), or a proligand (for the case with the asymmetrical ligand). Thus, three novel Eu(II) complexes, $Eu^{II}(L^{2,4,6\text{-Me3}})_2(THF)$ (**1**), $Eu^{II}(L^{2,6\text{-ipr2}})_2$ (**2**) and $Eu^{II}(L^{2,6\text{-ipr2}}{}_{Ph})_2$ (**5**), were prepared by the sterically induced reduction of Eu(III), which represents a new route for the synthesis of β-diketiminato Eu(II) complexes. The dimers of $(L^{2,4,6\text{-Me3}})_2$ (**3**) and $(L^{2,6\text{-ipr2}})_2$ (**4**) and the proligand $L^{2,6\text{-ipr2}}{}_{Ph}H$ (**6**) were also fully characterized. In addition we now report the possible mechanism for the sterically induced reduction of Eu(III).

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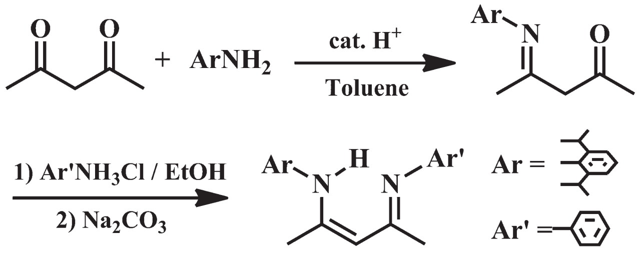
Results and Discussion

Synthesis of $L^{2,\,4,\,6\text{-Me3}}H$, $L^{2,\,6\text{-ipr2}}H$ and $L^{2,6\text{-ipr2}}_{Ph}H$

The following β-diketiminato ligands with varied substituents on the nitrogen atoms were chosen including $L^{2,\,4,\,6\text{-Me3}}H$, $L^{2,\,6\text{-ipr2}}H$ and $L^{2,\,6\text{-ipr2}}_{Ph}H$.

The proligands $L^{2,\,4,\,6\text{-Me3}}H$ and $L^{2,\,6\text{-ipr2}}H$ were prepared by the published method.[4] The new asymmetrical proligand $L^{2,\,6\text{-ipr}}_{Ph}H$ was synthesized by a similar procedure for the synthesis of asymmetrically substituted diimines.[5] The reaction of 2, 4-pentanedione with equivalent of 2, 6-diisopropyl-aniline in an acidic toluene solvent, followed by treatment with an equivalent of aniline hydrochloride in ethanol afforded the ligand $L^{2,\,6\text{-ipr}}_{Ph}H$ as pale yellow crystals upon crystallization from the n-hexane solution in 23% yield. (Scheme 1)



Scheme 1 Syntheses of $L^{2,\,6\text{-ipr}}_{Ph}H$.

Synthesis of $Eu^{II}(L^{2,\,4,\,6\text{-Me3}})_2(THF)$ (1) and $Eu^{II}(L^{2,\,6\text{-ipr2}})_2{\cdot}CH_3C_6H_5$ (2), and the dimers of $(L^{2,\,4,\,6\text{-Me3}})_2$ (3) and $(L^{2,\,6\text{-ipr2}})_2$ (4)

The reaction of anhydrous $EuCl_3$ with $NaL^{2,\,4,\,6\text{-Me3}}$ was conducted first. Treatment of a suspension of $EuCl_3$ in THF with a THF solution of $NaL^{2,\,4,\,6\text{-Me3}}$ in a molar ratio of 1 : 3 at 60 °C gave a red suspension. Removing the NaCl by centrifugation led to a red solution, from which $Eu^{II}(L^{2,4,6\text{-Me3}})_2(THF)$ (**1**) was isolated as red crystals in good yield upon crystallization (Scheme 2).

The elemental analysis of **1** is consistent with its formula. The IR spectra of **1** exhibited strong absorptions near 1551 and 1528 cm^{-1}, which were consistent with the partial C═N character of the β-diketiminato ligands.[6] However, a resolvable ^{1}HNMR spectrum could not be measured owing to paramagnetism. The identity of complex **1** was established by an X-ray structure determination.

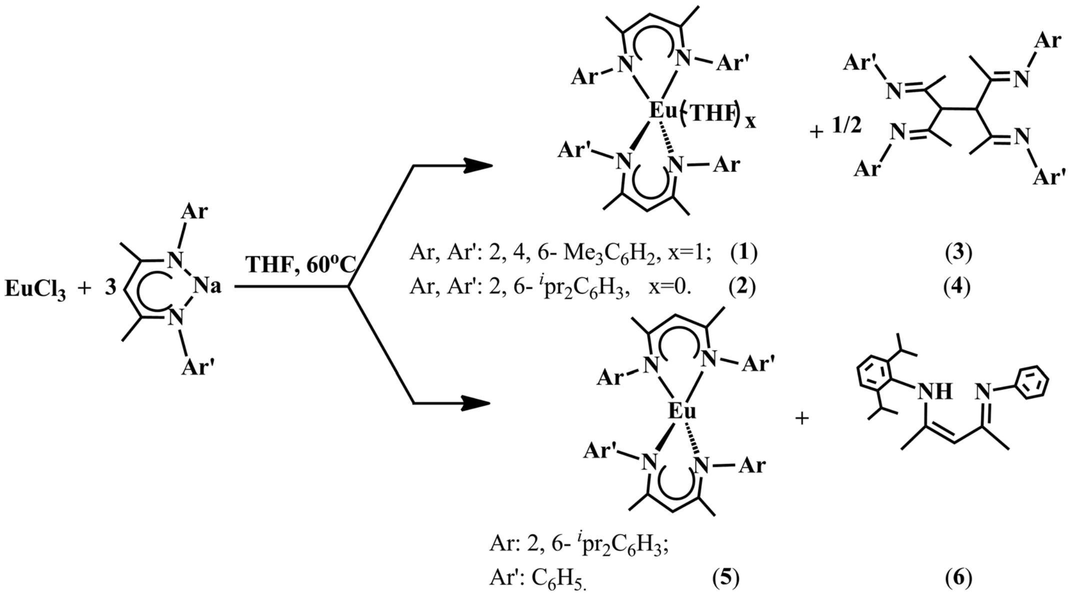
To further confirm the oxidation state of the central metal Eu in **1**, the BVS (Bond Valence Sum) calculation was made, as BVS could be used as a convenient method to estimate the oxidation state of a central metal in a complex.[7] The BVS for **1** equals 2.12, indicating Eu metal being in the 2+ oxidation state.

Replacement of the $NaL^{2,\,4,\,6\text{-Me3}}$ by the sodium salt of the bulkier ligand $NaL^{2,\,6\text{-ipr2}}$ in the above reaction also led to a red solution. Crystallization from the solution afforded the un-solvated complex $Eu^{II}(L^{2,\,6\text{-iPr2}})_2$ (**2**) as red crystals (Scheme 2). Complex **2** was characterized by satisfactory elemental analyses, IR spectra and an X-ray structure determination. But no resolvable ^{1}HNMR spectrum of **2** could be obtained as the in the case of **1**.

BVS calculation for **2** gave the value of 1.86, demonstrating the Eu metal in **2** being also 2+.

The formation of **1** and **2** indicates unequivocally that the reduction of Eu(III) occurred in both reactions, and the efficient reducing agent here might be the bulky anions of $L^{2,\,4,\,6\text{-Me3}}$ and $L^{2,\,6\text{-iPr2}}$, respectively, as mentioned previously.[2] Thus, the dimer of $L^{2,\,4,\,6\text{-Me3}}$ for the former reaction and the dimer of $L^{2,\,6\text{-iPr2}}$ for the latter one could be isolated as the other product. After the isolation of **1** or **2** was completed, the dimer of $(L^{2,\,4,\,6\text{-Me3}})_2$ (**3**) and the dimer of $(L^{2,\,6\text{-iPr2}})_2$ (**4**) were indeed obtained upon crystallization from each mother liquid (Scheme 2). However, the isolation of **4** is more difficult than that of **3**, as **4** is more soluble in organic solvents compared to **3**. Both **3** and **4** were identified by a crystal structure analysis (see the supporting information†).

Complexes **1** and **2** are sensitive to air and moisture, but are thermally stable up to their own melting point.



Scheme 2 Reaction of $EuCl_3$ with the sodium derivatives of the ligands.

Synthesis of [$Eu^{II}(L^{2,\ 6\text{-ipr2}}{}_{Ph})_2$] (5) and the proligand $L^{2,6\text{-ipr2}}{}_{Ph}H$ (6)

The success in the syntheses of complexes **1** and **2** from the above reactions encouraged us to further investigate the reaction of $EuCl_3$ with the sodium salt of asymmetrical β-diketiminato $NaL^{2,\ 6\text{-ipr2}}{}_{Ph}$ in a molar ratio of 1 : 3 at 60 °C in THF. The reaction went smoothly to give a red solution. After workup, the corresponding Eu^{II} complex [$Eu^{II}(L^{2,\ 6\text{-ipr2}}{}_{Ph})_2$] (**5**) was prepared as red crystals in reasonable yield (Scheme 2). The low yield of the crystals of **5** may be attributed to its very high solubility in organic solvents, even in n-hexane.

Complex **5** was fully characterized by elemental analysis, IR spectrum and an X-ray structure analysis. The oxidation state of the Eu metal in **5** was estimated by BVS calculation. The value of BVS equals 1.99.

It's unexpected that no dimer of $(L^{2,\ 6\text{-ipr2}}{}_{Ph})_2$ was isolated from the mother liquid, but the proligand $L^{2,\ 6\text{-ipr2}}{}_{Ph}H$ (**6**) was obtained instead (Scheme 2). The formation of **6** indicates oxidation of a β-diketiminato anion under the present condition could be realized in different ways (to a dimer or a proligand) depending on the β-diketiminato anion used.

The proligand **6** was characterized by an X-ray crystal structure analysis (see the supporting information†).

Molecular structures of 1, 2 and 5

The molecular structures of **1**, **2** and **5** are shown in Fig. 1, 2 and 3, respectively. Selected bond distances and angles are listed in Table 2.

The Eu(II) ion in **1** is ligated by four nitrogen atoms and one oxygen atom in a distorted trigonal bipyramid with the two nitrogen atoms of N1 and N3 and the three atoms of O1, N2 and N4, occupying two axial sites (the angle of N1–Eu1–N3, 160.08 (14)°) and the equatorial positions, respectively. The molecular structure of complex **1** is quite similar to that reported for $Eu^{II}(L^{2,\ 6\text{-Me2}})_2(THF)$.[2]

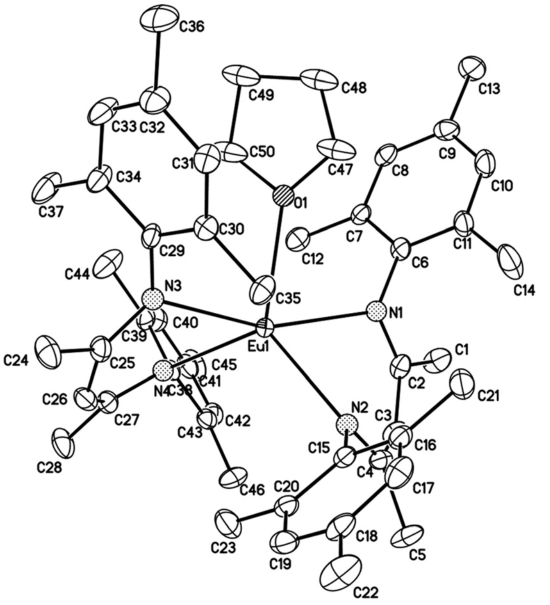


Fig. 1 ORTEP diagram of **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

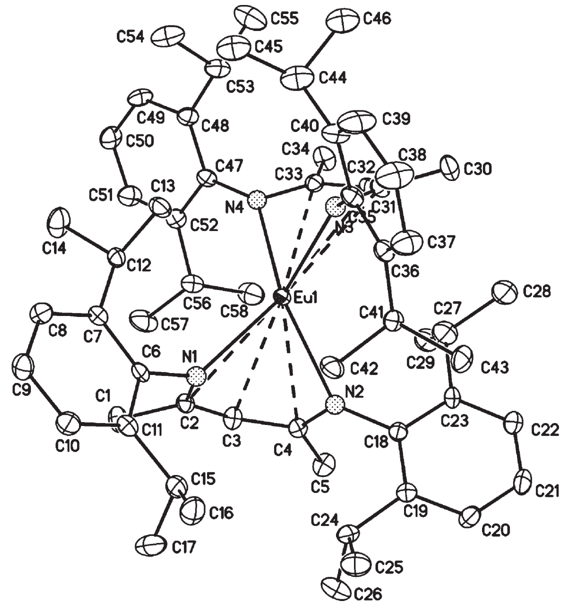


Fig. 2 ORTEP diagram of **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

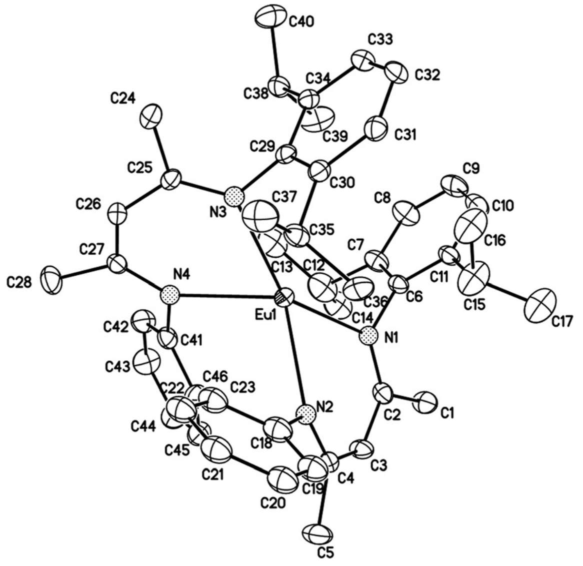


Fig. 3 ORTEP diagram of **5** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Each of the Eu(II) ions in **2** and **5** coordinates to four nitrogen atoms of the two ligands and the coordination geometry around each Eu ion is a tetrahedron, which is similar to that of $Yb^{II}(L^{Ph,\ Ph})_2$.[8] There is no coordinated THF molecule in both complexes. This might be because the coordination sphere around each Eu^{II} ion in **2** or **5** is crowded by two bulkier ligands $L^{2,\ 6\text{-ipr2}}$ or $L^{2,\ 6\text{-ipr2}}{}_{Ph}$, compared to $L^{2,4,6\text{-Me3}}$ in **1**. There is a

Table 1 Crystallographic data for complexes **1**, **2**, and **5**

	1	2	5
Expirical formula	C_{50} H_{66} Eu N_4 O	C_{58} $H_{82}N_4Eu{\cdot}C_7H_8$	C_{46} H_{58} Eu N_4
Formula weight	891.03	1079.37	818.92
T/K	223(2)	223(2)	223(2)
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	P $2_12_12_1$	P $2_12_12_1$	P $\bar{1}$
Flack parameters	0.013(11)	−0.009(12)	—
a/Å	11.5227(15)	12.4327(8)	10.9466(15)
b/Å	19.681(3)	19.2691(12)	11.5259(16)
c/Å	20.917(3)	24.7480(16)	19.195(2)
α (°)	90	90	101.515(2)
β (°)	90	90	96.956(2)
γ (°)	90	90	115.923(2)
V/Å^3	4743.5(12)	5928.8(7)	2073.8(5)
Z	4	4	2
$D_{\text{calcd.}}$ (mg cm^{-3})	1.248	1.209	1.311
Absorption coefficient (mm^{-1})	1.360	1.099	1.547
F(000)	1860	2284	850
θ range (°)	3.10–25.50	3.14–25.50	3.04–25.50
Reflections collected/ unique	15182/8384 [R(int) = 0.0385]	20443/10494 [R(int) = 0.0466]	17904/7668 [R(int) = 0.0576]
Data/restraints/ parameters	8384/10/516	10494/14/608	7668/0/419
Goodness-of-fit on F^2	1.033	1.096	1.121
Final R [$I > 2\sigma(I)$]	0.0416	0.0468	0.0726
wR_2 (all data)	0.0751	0.0927	0.1458

free toluene molecule in the unit cell of **2**, but no toluene molecule in **5**.

The bond parameters in both Eu-β-diketiminato units of each complex are almost constant. For example, each Eu–N bond distance and the angle of N–Eu–N in the two Eu–L units are 2.534(4) Å, 2.542(4) Å and 75.44(13)°, 2.528(4) Å, 2.563(4) Å and 73.95(14)° for **1**; 2.496(4) Å, 2.545(4) Å and 76.52(13)°, 2.499(4) Å, 2.555(4) Å and 77.74(14)° for **2**; 2.496(5) Å, 2.502(6) Å and 75.39(18)°, 2.487(6) Å, 2. 506(5) Å and 74.53(18)° for **5**, respectively. This structural feature is the same as that found in $Yb^{II}(L^{Ph,\ Ph})_2$ ($L^{Ph,\ Ph}$ = [N(SiMe$_3$)C(Ph)C(H)C(Ph)N(SiMe$_3$)$_2$])[8] and $Eu^{II}(L^{2,\ 6\text{-Me2}})_2$(THF).[2] The average Eu–N distance in each complex (2.542(4) Å for **1**; 2.524(4) Å for **2**; 2.498(6) Å for **5**) is longer than the 2.467(9) Å found in the trivalent complex $Eu(L^{2\text{-Me}})_3$ ($L^{2\text{-Me}}$ = [N(2-MeC$_6$H$_4$)C(Me)]$_2$CH),[2] in agreement with the difference in Eu3+ and Eu2+ ionic radii, but can be compared with that found in $Eu^{II}(L^{2,\ 6\text{-Me2}})_2$(THF) (2.557(4) Å).[2]

However, the influence of the size of the β-diketiminato ligand on the bonding mode of a β-diketiminato to a Eu(II) ion in **1**, **2** and **5** is observed. Both $L^{2,\ 6\text{-ipr2}}$ ligands in **2** coordinate to the Eu(II) ion in a close η^5 mode (Fig. 2). The distances of Eu–C (β-diketiminato) bonds range from 3.044(5) Å to 3.131(57) Å, which are within the upper limit for significant intramolecular π-arene···Ln interactions.[9] The dihedral angle between the N1–Eu–N2 and N1–C2–C4–N2 planes is 69.984° in **2** (67.5° in the η^5-bonded [Yb{N(SiMe$_3$)C-(C$_6$H$_4$Me-4)CHC-(adamantyl-1)N(SiMe$_3$)}$_2$]).[8] Whilst, each ligand in **1** ($L^{2,\ 4,\ 6\text{-Me3}}$) and **5** ($L^{2,\ 6\text{-ipr2}}{}_{Ph}$) coordinates to the Eu(II) ion in a κ^2 mode, the distances of Eu(II) to C atoms (β-diketiminato) all are far from the upper limit for significant intramolecular π-arene···Ln interactions (Table 2). The dihedral angle between the N1–Eu–N2 and N1–C2–C4–N2 planes is 48.534° in **1** and 21.159° in **5** (10.8° in the κ^2-bonded [Yb(L′)$_2$]).[8]

Possible mechanism for the reduction of a Eu^{III} ion to a Eu^{II} ion

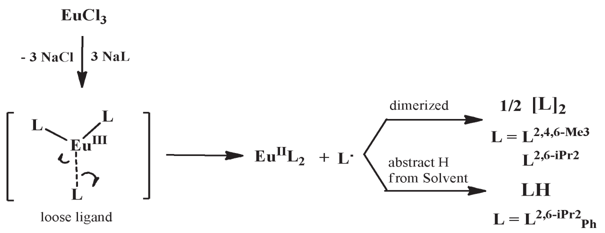
The reduction reaction of Ln(III) ions has not been observed in the preparation of tris β-diketiminato Eu complexes with the less bulky β-diketiminato ligand,[2] although the reduction reaction of $Cp_3Eu{\cdot}THF$ or $Cp_2EuCl{\cdot}THF$ with Li-naphthalene reagent was reported,[10] indicating the sodium salt of β-diketiminato, in general, could not be used as an efficient reducing agent. The reduction of Eu(III) here should result from sterically induced reduction as in the cases with the formation of $Eu^{II}(L^{2,\ 6\text{-Me2}})_2$(THF) reported previously[2] and the formation of ((4-nBu-C$_6$H$_4$)$_5$C$_5$)$_2$Ln (Ln=Yb, Sm) from the reaction of (2-Me$_2$N-benzyl)$_3$Ln with (4-nBu-C$_6$H$_4$)$_5$C$_5$H reported by Harder[11] The sterically induced reduction has been well documented by Evans[12] in the reduction chemistry of the sterically demanding $(Cp^{BIG})_3$Ln. A similar mechanism to that proposed for the reduction reactivity of $(Cp^{BIG})_3$Ln (Ln = Yb, Sm) can be used to explain the reduction of Eu(III) by β-diketiminato anions in a overcrowded tris-β-diketiminato Eu(III) transient. The reaction of EuCl$_3$ with NaL (L = $L^{2,\ 4,\ 6\text{-Me3}}$, $L^{2,\ 6\text{-ipr2}}$ and $L^{2,\ 6\text{-ipr2}}{}_{Ph}$) affords an unstable [LnL$_2$…L] with a loose L farther from the Eu(III) ion than their usual optimal distance. The loose L anion in the transient is not electro-statically stabilized as effectively as it is in conventional β-diketiminato complexes. Thus, the unstable [LnL$_2$…L] transfers to a stable Eu(II) complex (**1**, **2** or **5**) and a L radical($L^{2,\ 4,\ 6\text{-Me3}}\cdot$, $L^{2,\ 6\text{-ipr2}}\cdot$ or $L^{2,\ 6\text{-ipr2}}{}_{Ph}\cdot$) *via* giving up an electron by the loose L anion to the Eu^{III} ion (Scheme 3). The resulting radical dimerizes to a dimer or picks up a H atom from the solvent to a proligand immediately. The proposed pathway is confirmed by the isolation of dimers of **3** and **4** and proligand **6**. The only difference in the mechanism between our cases and the reduction reactivity of (C$_5$Me$_5$)$_3$Ln is that the ligand anion gives up an electron to the Eu(III) ion in our cases and to the substrate in their cases. Efforts to isolate the unstable intermediate have not been successful yet.

Conclusions

Divalent complexes **1**, **2** and **5** were synthesized in good yields by the metathesis reaction of EuCl$_3$ with three equivs of sodium salt of bulky β-diketiminato NaL (L = $L^{2,\ 4,\ 6\text{-Me3}}$, $L^{2,\ 6\text{-ipr2}}$ and $L^{2,\ 6\text{-ipr2}}{}_{Ph}$). The reduction reaction proceeds mechanistically through a sterically induced reduction pathway: the L anion in the overcrowded L$_3$Eu(III) transient gives up an electron to the Eu^{III} ion leading to the formation of the corresponding Eu(II) complex and the L radical, which either dimerizes to a dimer or picks up a H atom from solvent to a proligand. Further study on the reactivity of β-diketiminato ligand in a sterically demanding complex is now underway.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**, **2**, and **5**

Bond lengths	**1**	**5**	Bond lengths	**2**
Ln(1)–N(1)	2.542(4)	2.496(5)	Ln(1)–N(1)	2.496(4)
Ln(1)–N(2)	2.534(4)	2.502(6)	Ln(1)–N(2)	2.545(4)
Ln(1)–N(3)	2.563(4)	2.506(5)	Ln(1)–N(3)	2.499(4)
Ln(1)–N(4)	2.528(4)	2.487(6)	Ln(1)–N(4)	2.555(4)
(Ln–N)av.	2.542(4)	2.498(6)	(Ln–N)av.	2.524(4)
Ln(1)–O(1)	2.542(3)	—	Ln(1)–O(1)	—
Ln(1)…C(2)	3.337(61)	3.478(62)	Ln(1)…C(2)	3.044(5)
Ln(1)…C(3)	3.524(59)	3.783(59)	Ln(1)…C(3)	3.131(57)
Ln(1)…C(4)	3.343(56)	3.487(61)	Ln(1)…C(4)	3.118(5)
Ln(1)…C(25)	3.426(60)	3.507(50)	Ln(1)…C(31)	3.053(4)
Ln(1)…C(26)	3.661(59)	3.829(62)	Ln(1)…C(32)	3.103(56)
Ln(1)…C(27)	3.436(59)	3.520(74)	Ln(1)…C(33)	3.086(6)
C(1)–C(2)	1.523(7)	1.519(10)	C(1)–C(2)	1.524(7)
N(1)–C(2)	1.331(7)	1.319(8)	N(1)–C(2)	1.312(7)
C(2)–C(3)	1.402(7)	1.409(10)	C(2)–C(3)	1.419(8)
C(3)–C(4)	1.392(9)	1.389(10)	C(3)–C(4)	1.410(7)
N(2)–C(4)	1.335(7)	1.340(8)	N(2)–C(4)	1.332(6)
C(4)–C(5)	1.538(7)	1.503(10)	C(4)–C(5)	1.508(7)
C(24)–C(25)	1.506(8)	1.511(9)	C(30)–C(31)	1.522(7)
N(3)–C(25)	1.325(7)	1.309(8)	N(3)–C(31)	1.310(7)
C(25)–C(26)	1.414(8)	1.422(9)	C(31)–C(32)	1.426(8)
C(26)–C(27)	1.375(9)	1.399(10)	C(32)–C(33)	1.425(8)
N(4)–C(27)	1.339(7)	1.331(9)	N(4)–C(33)	1.337(6)
C(27)–C(28)	1.528(7)	1.510(9)	C(33)–C(34)	1.520(7)
Bond angles			Bond angles	
N(2)–Eu (1)–N(4)	115.00(14)	105.64(18)	N(2)–Eu (1)–N(4)	137.55(14)
N(2)–Eu(1)–N(1)	75.44(13)	75.39(18)	N(2)–Eu(1)–N(1)	76.52(13)
N(4)–Eu(1)–N(1)	118.11(14)	121.35(19)	N(4)–Eu(1)–N(1)	122.69(14)
N(2)–Eu(1)–N(3)	115.33(14)	133.27(18)	N(2)–Eu(1)–N(3)	122.41(13)
N(4)–Eu(1)–N(3)	73.95(14)	74.53(18)	N(4)–Eu(1)–N(3)	77.74(14)
N(1)–Eu(1)–N(3)	160.08(13)	145.55(18)	N(1)–Eu(1)–N(3)	128.37(14)
(N–Eu–N)av.	109.65(14)	109.29(18)	(N–Eu–N)av.	110.88(14)



Scheme 3 The possible mechanism for the reduction pathway.

Experimental Section

General Procedures

All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. The proligands $L^{2,\ 4,\ 6\text{-Me3}}H$ and $L^{2,\ 6\text{-ipr2}}H$ were prepared by the published method.[4] Anhydrous $LnCl_3$ was prepared according to the literature procedure.[13] Lanthanide analyses were performed by ethylenediaminetetraacetic acid (EDTA) titration with a xylenol orange indicator and a hexamine buffer.[14] Solvents were degassed and distilled from sodium benzophenone ketyl before use. Element analyses were performed by direct combustion using a CarloErba 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 a sealed Ar-filled capillary.

Preparation

$L^{2,\ 6\text{-ipr}}_{Ph}H$. To a mixture of 2, 6-diisopropyl-aniline (100 mmol) and acetylacetone (100 mmol) in toluene (150 mL) was added *p*-toluenesulfonic acid (0.3 g). The reaction mixture was refluxed for 24 h to remove water by the oil–water separator, and then cooled to ambient temperature. Removing toluene led to a precipitate and then $PhNH_3Cl$ (100 mol) and EtOH (150 mL) were added. The resulting solution was refluxed for 24 h, and then cooled to ambient temperature. The undissolved portion was removed by filtration and the yellow solution was evaporated to dryness. The residue was treated with ether (150 mL) and a saturated aqueous solution of Na_2CO_3. The mixture was stirred for 4 h, and then extracted with ether (30 mL) 3 times. The combined organic layers were dried with $MgSO_4$, and then the solvent was evaporated. The residue was dissolved in a small amount of n-hexane to afford a yellow solution. Crystallization at −20 °C gave colorless crystals of $L^{2,\ 6\text{-ipr}}_{Ph}H$. Yield: 7.73 g (23.1%). m.p. 87.5–88.3 °C (decomp.). ^{1}HNMR (300 MHz, $CDCl_3$) δ = 12.65 (1 H, s, N*H*), 7.21 (2 H, d, *J* 8.6, Ar*H*), 7.08 (3 H, s, Ar*H*), 6.97 (1H, t, *J* = 7.4 Hz, Ar*H*), 6.89 (2 H, d, *J* = 7.4 Hz Ar*H*), 4.83 (1 H, s, C*H*), 2.95 (2 H, dt, *J* 13.7, 6.9, C*H*-$(CH_3)_2$), 2.02 (3 H, s, C*H*$_3$-C═N), 1.65 (3 H, s, C*H*$_3$-C═N), 1.12 (12 H, dd, *J* 22.1, 6.9, CH-(C*H*$_3$)$_2$).^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.37 (*C*═N), 157.87 (*C*═N), 145.31 (Ar), 143.01 (Ar), 141.66 (Ar), 129.48 (Ar), 125.25 (Ar), 123.64 (Ar), 123.19 (Ar), 120.52 (Ar), 96.53 (C(N)-*C*H-C(N)), 28.98 (*C*H-$(CH_3)_2$), 24.89 (*C*H$_3$-C═N), 23.37

(CH_3-C=N), 21.72 (CH-(CH_3)$_2$), 21.48 (CH-(CH_3)$_2$). $C_{23}H_{30}N_2$ (334.49): calcd. C, 82.59; H, 9.04; N, 8.37; found C, 82.37; H, 9.17; N, 8.46. IR(KBr): 3059 (w), 2961 (w), 2919 (w), 2864 (w), 1937(w), 1870 (w), 1801(w),1738(w), 1629 (s), 1553 (s), 1485 (w), 1361 (m), 1273 (m), 1175 (m), 1175 (s), 1101 (w), 1022 (w), 801 (s), 791 (s), 751 (s), 696 (m), 597 (w), 507 (w), 424(m) cm^{-1}.

Eu($L^{2,\ 4,\ 6\text{-Me3}}$)$_2$(THF) (1) and ($L^{2,\ 4,\ 6\text{-Me3}}$)$_2$ ·C_6H_{14} (3). A THF solution of $NaL^{2,\ 4,\ 6\text{-Me3}}$ (26.6 mL, 0.489 M) which was formed by reaction of $L^{2,\ 4,\ 6\text{-Me3}}H$ with NaH in THF was added to a slurry of anhydrous $EuCl_3$ (1.12 g, 4.34 mmol) in THF (about 20 mL) at room temperature. The reaction mixture was stirred at 60 °C for 24 h. After the undissolved portion was removed by centrifugation, the red solution was concentrated to dry then about 0.5 mL THF and 6 mL n-hexane were added. Crystallization at room temperature afforded red crystals **1** (2.59 g, 67%). $C_{50}H_{66}EuN_4O$ (891.03): calcd. C 67.40, H 7.47, N 6.29, Eu 17.05; found C 66.88, H 7.33, N 6.67, Eu 17.43. m. p. 109.1–111.5 °C (decomp.). IR (KBr): 2916 (m), 2856 (w), 2727 (w), 1623 (s), 1552 (s), 1476 (s), 1433 (w), 1274 (m), 1187 (m), 1146 (m), 1027 (w), 853 (s), 795 (w), 598 (w), 563 (w), 492 (w) cm^{-1}. After the isolation of complex **1** was complete, the mother liquid of reaction was concentrated and 4 mL n-hexane was added. Pale-yellow microcrystals of **3** were obtained at −20 °C after several days.

Eu($L^{2,\ 6\text{-ipr2}}$)$_2$·$CH_3C_6H_5$ (2) and ($L^{2,\ 6\text{-ipr2}}$)$_2$ (4). These were obtained by the same procedure as that for complex **1**, except that $EuCl_3$ (0.81 g, 3.14 mmol) and $NaL^{2,\ 6\text{-ipr2}}$ (16.8 mL, 0.561 M), which was formed by reaction of $L^{2,\ 6\text{-ipr2}}H$ with NaH in THF, were used. Complex **2** was first crystallized from a toluene (3 mL) solution. However, no crystals could be obtained. Thus, the toluene was evaporated to oil, into which was added a mixture of 0.5 mL THF and 4 mL n-hexane. Crystallization at room temperature afforded red crystals **2** (1.39 g, 41%). $C_{58}H_{82}N_4Eu{\cdot}C_7H_8$ (1079.37): calcd. C 72.33, H 8.40, N 5.19, Eu 14.08; found C 71.35, H 8.46, N 5.89, Eu 14.56. m. p. 111.1–130.2 °C. IR (KBr): 3060 (w), 2961 (s), 2927 (m), 2868 (m), 1660 (m), 1622 (s), 1550 (s), 1462 (m), 1439 (m), 1381 (m), 1362 (m), 1276 (m), 1175 (m), 1057 (m), 934 (w), 788 (m), 759 (m), 696 (w), 599 (w), 429 (w) cm^{-1}. After the isolation of complex **2** was complete, the mother liquid of reaction was concentrated and 10 mL n-hexane was added. Pale-yellow microcrystals of **4** were obtained at −20 °C after several days.

Eu($L^{2,\ 6\text{-ipr2}}{}_{Ph}$)$_2$ (5) and $L^{2,\ 6\text{-ipr2}}{}_{Ph}H$ (6). By the same procedure as that for complex **1**, red crystals of complex **5** (0.62 g, 23%) were obtained from the reaction of $EuCl_3$ (0.86 g, 3.33 mmol) with $NaL^{2,\ 6\text{-ipr2}}{}_{Ph}$ (21.7 mL, 0.460 M), which was formed by reaction of $L^{2,\ 6\text{-ipr2}}{}_{Ph}H$ with NaH in THF upon crystallization from a mixture of 0.5 mL THF and 5 mL n-hexane at room temperature. $C_{46}H_{58}EuN_4$ (818.92): calcd. C 67.46, H 7.14, N 6.84, Eu 18.56; found C 67.08, H 7.33, N 6.61, Eu 18.41. m.p. 115.7–118.1 °C (decomp.). IR(KBr): 3057 (w), 2960 (m), 2924 (w), 2866 (w), 1626 (s), 1553 (s), 1485 (w), 1362 (m), 1278 (m), 1176 (m), 1101 (w), 1026 (w), 791 (m), 750 (m), 699 (m), 597 (w), 508 (w) cm^{-1}. After the isolation of complex **5** was complete, the mother liquid of reaction was concentrated and 3 mL n-hexane was added. Pale-yellow crystals of **6** were obtained at −20 °C after several days.

X-ray Crystallography

Suitable single crystals of compounds **1–6** 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 ω scan mode by using Mo-Kα radiation (λ = 0.71075 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption. Details of the intensity data collection and crystal data are given in Table 1. 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 SHELXL-97 program. CCDC 843447 (for **1**), 843448 (for **2**), 843449 (for **3**), 843450 (for **4**), 843451 (for **5**) and 843452 (for **6**) are contained in 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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