

Synthesis, Reactivity and Crystal Structure of β -Diketiminato Ytterbium Chlorides

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Reaction of anhydrous YbCl₃ with 1 equiv. of LLi [L=*p*-ClPhNC(Me)CH(Me)N(C₆H₃-2,6-*i*-Pr₂)] in THF at room temperature gave the β -diketiminato lanthanide dichloride LYbCl₂(THF)₂ (**1**) in good isolated yield. Similarly reaction of anhydrous YbCl₃ with 1 equiv. of LLi, then with 1 equiv. of *t*-BuCpNa in THF yielded the expected mixed-ligand β -diketiminato ytterbium chloride (*t*-BuCp)YbL(μ -Cl)₂Li(THF)₂ (**2**). Both **1** and **2** were well characterized by elemental analysis, IR spectra, ¹H NMR spectra, and X-ray diffraction analysis.

Keywords lanthanide complex, β -diketiminato ligand, synthesis, reactivity, crystal structure

Introduction

β -Diketiminates have several attractive features: their monoanions are iso-electronic to cyclopentadienyl anions, their steric and electronic properties can be easily tuned, and their coordination bonding models may range from purely σ to a combination of σ and π donation.¹ In particular, some β -diketiminato complexes have found potential applications as homogeneous polymerization catalysts. For example, β -diketiminato zinc(II) complexes can catalyze the alternating copolymerization of CO₂ and epoxides,² cationic β -diketiminato scandium methyl complexes have ethylene polymerization activities comparable to those of metallocenes, *etc.*³ As a result, these ligands have attracted considerable attention in recent years for preparation of organometallic complexes across the periodic table.¹

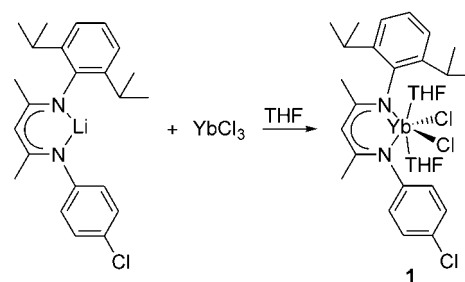
We have recently reported that β -diketiminato anion [(C₆H₃-2,6-*i*-Pr₂)NC(Me)CH(Me)N(C₆H₃-2,6-*i*-Pr₂)]⁻ is an ideal ligand for preparation of mixed-ligand lanthanide chlorides, which are important precursors for synthesizing the corresponding alkyl and amido complexes.⁴ As our extensive study in this area and to understand the relationship between the coordination environment around metal center and their reactivity, we synthesized and characterized lanthanide complexes with asymmetric β -diketiminato ligand L [L=*p*-ClPhNC(Me)CH(Me)N(C₆H₃-2,6-*i*-Pr₂)], LYbCl₂(THF)₂ (**1**) and (*t*-BuCp)YbL(μ -Cl)₂Li(THF)₂ (**2**). Here we report these results.

Results and discussion

Synthesis of LYbCl₂(THF)₂ (**1**) and (*t*-BuCp)YbL(μ -Cl)₂Li(THF)₂ (**2**)

The metathesis reaction between anhydrous YbCl₃ and freshly prepared LLi proceeds smoothly at room temperature, and gives the desired red product **1** in 67% isolated yield as shown in Scheme 1.

Scheme 1



Complex **2** can be obtained by the reaction of one equiv. of *t*-BuCpNa with **1** formed *in situ* between YbCl₃ and LLi in THF at room temperature (Scheme 2). After crystallizing from THF/hexane (1 : 1, V : V) mixture solution, **2** was isolated as orange-red needle crystals in 46% yield.

Both complexes were characterized by elemental analysis, FT-IR, ¹H NMR spectroscopy, and X-ray diffraction analysis. The IR spectra exhibit strong absorp-

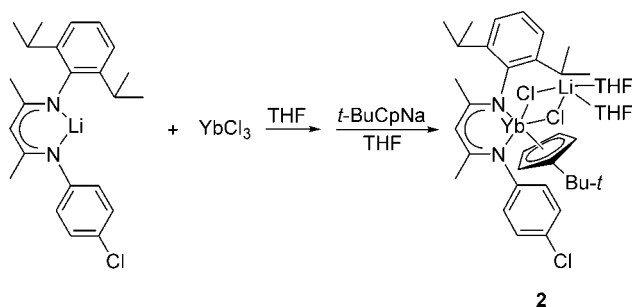
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tions near 1550 and 1530 cm^{-1} , which are consistent with partial C=N double bond character.⁵ Complex **1** is slightly sensitive to air and moisture, and its crystals can be exposed in air for a few hours without apparent decomposition, while complex **2** is quite sensitive to air and moisture. They are well soluble in THF, moderate soluble in aromatic solvents, and insoluble in aliphatic hydrocarbons.

Scheme 2



Crystal structures of **1** and **2**

The molecular structure of complex **1** is shown in Figure 1, and the selected bond lengths and angles are listed in Table 1. Complex **1** has a monomeric structure in the solid state. The two THF molecules are disordered due to strong thermal motion. The ytterbium atom is six-coordinated with two nitrogen atoms of the β -diketiminato ligand, two chlorine atoms, and two THF molecules in a distorted octahedron geometry. The molecular structure establishes *cis* disposition of the THF molecules, and *trans* disposition of the chlorine atoms.

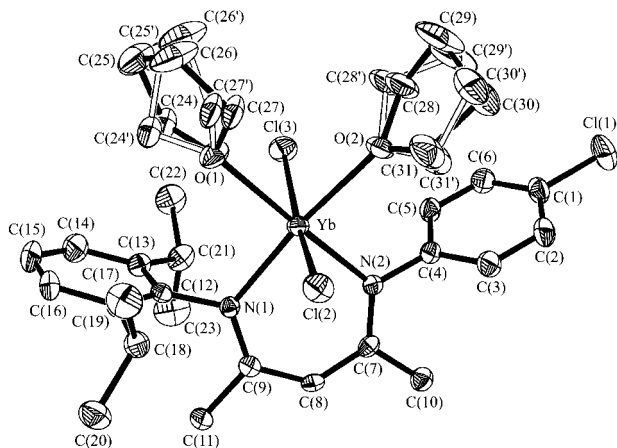


Figure 1 Molecular structure of $\text{LYbCl}_2(\text{THF})_2$ (**1**).

The β -diketiminato ligand is symmetrically coordinated to the ytterbium ion with the variation in Yb—N bond lengths of 0.0021 nm [0.2313(3) and 0.2292(3) nm, respectively], which is similar to that found in $[\text{PhNC}(\text{Me})\text{CH}(\text{Me})\text{NPh}]\text{GdBr}_2(\text{THF})_2$ ⁶ and $[p\text{-ClPhNC}(\text{Me})\text{CH}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{-Pr}_2)]\text{SmCl}_2(\text{THF})_2$,⁷ but different from that in $[(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{-Pr}_2)\text{NC}(\text{Me})\text{CH}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{-Pr}_2)]\text{ScCl}_2(\text{THF})$, in which two nitrogen atoms are asymmetrically coordinated to the central

metal.⁸ The two Yb—Cl bond lengths of 0.25283(12) and 0.25410(11) nm are much longer than the corresponding one (0.2505(2) nm) in $[(\text{DIPPh})_2\text{nacnac}]\text{YbCl}(\mu\text{-Cl})_3\text{Yb}[(\text{DIPPh})_2\text{nacnac}](\text{THF})$.⁴ The bond lengths of C(7)—C(8), C(8)—C(9), N(1)—C(9) and N(2)—C(7) lie intermediate between the corresponding single- and double-bond distances (see Table 1), suggesting that π electrons are significantly delocalized within the β -diketiminato backbone. The Yb—C(7, 8, 9) distances are quite long, and it is suggested that the π contribution of the β -diketiminato ligand to Yb ion is negligible, and thus the β -diketiminato ligand is coordinated to central metal in a purely η^2 manner.

Table 1 Selected bond lengths (10^{-1} nm) and angles ($^\circ$) for complex **1**

Yb—N(2)	2.292(3)	Yb—Cl(3)	2.5410(11)
Yb—N(1)	2.313(3)	N(1)—C(9)	1.342(5)
Yb—O(1)	2.357(3)	N(2)—C(7)	1.328(4)
Yb—O(2)	2.365(3)	C(7)—C(8)	1.404(5)
Yb—Cl(2)	2.5283(12)	C(8)—C(9)	1.389(5)
N(2)—Yb—N(1)	82.27(11)	N(1)—Yb—Cl(3)	97.47(8)
N(2)—Yb—O(1)	174.82(10)	O(1)—Yb—Cl(3)	82.41(8)
N(1)—Yb—O(1)	97.79(10)	O(2)—Yb—Cl(3)	86.24(7)
N(2)—Yb—O(2)	92.81(11)	Cl(2)—Yb—Cl(3)	167.58(4)
N(1)—Yb—O(2)	173.94(10)	C(9)—N(1)—Yb	124.1(3)
O(1)—Yb—O(2)	87.42(10)	C(12)—N(1)—Yb	117.1(2)
N(2)—Yb—Cl(2)	95.63(8)	C(7)—N(2)—Yb	126.5(3)
N(1)—Yb—Cl(2)	92.97(7)	N(2)—C(7)—C(8)	123.0(4)
O(1)—Yb—Cl(2)	89.54(8)	C(9)—C(8)—C(7)	132.5(4)
O(2)—Yb—Cl(2)	83.95(7)	N(1)—C(9)—C(8)	124.4(4)
N(2)—Yb—Cl(3)	92.44(8)		

The N(1)—Yb(1)—N(2) angle is $82.27(11)^\circ$, which is more acute than the corresponding angle in $[(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{-Pr}_2)\text{NC}(\text{Me})\text{CH}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{-Pr}_2)]\text{ScCl}_2(\text{THF})$ ($86.77(17)^\circ$),⁸ and it is greater than that found in $[p\text{-ClPhNC}(\text{Me})\text{CH}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{-}2,6\text{-}i\text{-Pr}_2)]\text{SmCl}_2(\text{THF})_2$ ($77.54(9)^\circ$).⁷

The molecular structure of complex **2** is shown in Figure 2, and selected bond distances and angles are listed in Table 2. Complex **2** is a lithium chloride stabilized mixed-ligand ytterbium chloride. The coordination sphere of the Yb center is composed of two nitrogen atoms of a β -diketiminato ligand, a *tert*-butylcyclopentadienyl group, and two μ -chlorine atoms to display a distorted pyramidal geometry with Cl(1), Cl(2), N(1), and N(2) forming the base planar, and the Cp centroid being the vertex. The formal coordination number of the central metal is seven.

In complex **2**, the β -diketiminato ligand has some η^5 -character. The Yb—C(2, 3, 4) distances are 0.2796(5), 0.2899(5) and 0.2946(6) nm, respectively, which are

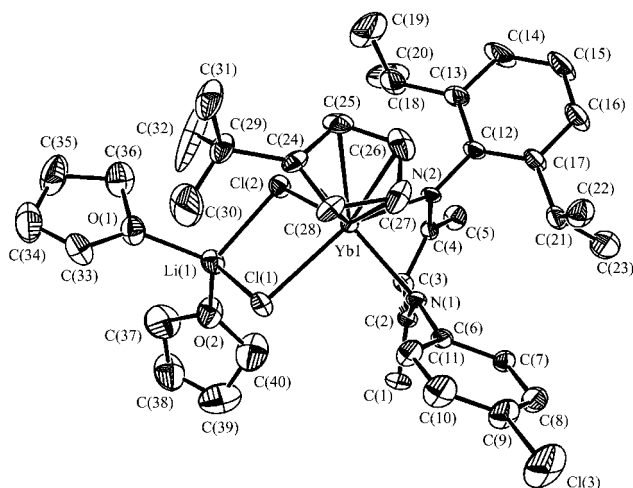


Figure 2 Molecular structure of (*t*-BuCp)YbL(μ -Cl)₂Li(THF)₂ (**2**).

Table 2 Selected bond lengths (10⁻¹ nm) and angles (°) for complex **2**

Yb(1)—Cl(1)	2.6658(15)	Yb(1)—C(27)	2.575(6)
Yb(1)—Cl(2)	2.6360(15)	Yb(1)—C(28)	2.628(6)
Yb(1)—N(1)	2.262(4)	Yb—C(av) ^a	2.624(6)
Yb(1)—N(2)	2.336(4)	Yb—Cent(1) ^a	2.334
Yb(1)—C(2)	2.796(5)	C(2)—C(3)	1.390(8)
Yb(1)—C(3)	2.899(5)	C(3)—C(4)	1.420(8)
Yb(1)—C(4)	2.946(6)	Cl(1)—Li(1)	2.366(12)
Yb(1)—C(24)	2.680(5)	Cl(2)—Li(1)	2.373(12)
Yb(1)—C(25)	2.640(6)	O(1)—Li(1)	1.928(13)
Yb(1)—C(26)	2.597(6)	O(2)—Li(1)	1.916(12)
Cl(1)—Yb(1)—Cl(2)	81.61(5)	Yb(1)—N(1)—C(2)	98.4(3)
Cl(1)—Yb(1)—N(1)	84.24(11)	Yb(1)—N(2)—C(4)	104.2(3)
Cl(2)—Yb(1)—N(1)	133.95(12)	Cl(1)—Li(1)—Cl(2)	94.0(4)
Cl(1)—Yb(1)—N(2)	141.58(11)	Cl(1)—Li(1)—Cl(2)	94.0(4)
Cl(2)—Yb(1)—N(2)	86.99(11)	O(1)—Li(1)—O(2)	105.1(6)
N(1)—Yb(1)—N(2)	77.66(15)		

^a Cent(1) is the center of ring C(24)—C(28).

well comparable with the Yb—C bond distances in the indisputably π -arene bonded complexes Yb(η^6 -C₆Me₆)-(AlCl₄)₃(MeC₆H₅)⁹ and [Yb(Odpp)₃]₂ (Odpp = 2,6-diphenylphenolate).¹⁰ This indicates that the complex involves π coordination of the β -diketimate ligand to the ytterbium atom, and there exists the combination of σ and π bonding modes of ligand to metal center, which is similar to that found in (MeCp)[(C₆H₃-2,6-*i*-Pr₂)NC(Me)CH(Me)N(C₆H₃-2,6-*i*-Pr₂)]YbCl.⁴

Different to that in complex **1**, the β -diketimate ligand in complex **2** is asymmetrically coordinated to the ytterbium ion, for the Yb(1)—N(1) length (0.2262(4) nm) is about 0.0074 nm shorter than the Yb(1)—N(2) length (0.2336(4) nm). The Yb—C(ring) distances range from 0.2575(6) to 0.2680(5) nm. The average Yb

—C(ring) distance of 0.2624(6) nm is about 0.004 nm longer than that in [(C₅H₅)₂YbCl]₂ (0.258(6) nm),¹¹ and is comparable with that in (C₅Me₅)₂Yb(μ -Cl)₂Li(Et₂O)₂ (0.2610(3) nm).¹² The Yb—Cl bond lengths of 0.26658(15) and 0.26360(15) nm are apparently longer than those in (C₅Me₅)₂Yb(μ -Cl)₂Li(Et₂O)₂,¹² suggesting that the steric repulsion plays a very important role.

Conclusion

We have shown that β -diketimate anion [*p*-ClPhNC(Me)CH(Me)N(C₆H₃-2,6-*i*-Pr₂)]⁻ is an ideal nitrogen-based ligand for the preparations of both lanthanide dichloride and mixed-ligand lanthanide monochloride, which are useful precursors for further transformation to obtain corresponding alkyl and amido complexes. In two complexes, the β -diketimate ligand adopts different coordination modes depending on the steric environment around the central metal.

Experimental

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl prior to use. Anhydrous YbCl₃,¹³ LLi⁷ and *t*-BuCpNa¹⁴ were prepared according to the reported procedures. Melting points were determined in argon-filled capillary tubes and are uncorrected. Lanthanide metal analyses were carried out by complexometric titration. The content of lithium was determined on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations. The IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer. ¹H NMR spectra were obtained using a Unity Inova-400 spectrometer.

Synthesis of LYbCl₂(THF)₂ (**1**)

A solution of LLi (50 mL, 5.80 mmol) in THF/hexane (2 : 3, V : V) was slowly added to a suspension of YbCl₃ (1.62 g, 5.80 mmol) in 50 mL of THF at room temperature. The color of the reaction solution gradually changed to red. The reaction mixture was then stirred for 48 h at room temperature. After centrifugation, the wine-red supernatant was concentrated to about 30 mL. Placing at room temperature overnight yielded red cubic crystals of **1** (3.3 g, 67%). m.p. 179—181 °C; ¹H NMR (C₆D₆, 400 MHz) δ : 6.53—7.41 (m, 7H, aromatic protons), 4.88 (s, 1H, CH=C(CH₃)N), 3.90—3.76 (m, 8H, THF- α -CH₂), 3.21—3.04 (m, 2H, CH(CH₃)₂), 1.77 (s, 3H, CH₃), 1.65 (s, 3H, CH₃), 1.59—1.43 (m, 8H, THF- β -CH₂), 1.24 (d, *J*=8 Hz, 6H, CH(CH₃)₂), 1.17 (d, *J*=5.2 Hz, 6H, CH(CH₃)₂); IR (KBr) ν : 3422, 2963, 2866, 1628, 1539, 1485, 1396, 1327, 1277, 1172, 1046, 895, 783, 679 cm⁻¹. Anal. calcd for C₃₁H₄₄Cl₃N₂O₂Yb: C 49.24, H 5.87, N 3.71, Yb 22.89; found C 48.64, H 5.91, N 3.76, Yb 22.64.

Synthesis of (*t*-BuCp)YbL(μ -Cl)₂Li(THF)₂ (2**)**

To a slurry of anhydrous YbCl₃ (1.12 g, 3.99 mmol) in 50 mL of THF was slowly added the solution of LLI (50 mL, 3.99 mmol) in THF/hexane (2 : 3, *V* : *V*) at room temperature. After YbCl₃ disappeared completely, a THF solution of *t*-BuCpNa (36.4 mL, 4.00 mmol) was added slowly via a syringe. The mixture was stirred at room temperature for another 48 h, and then NaCl was removed by centrifugation. The wine-red supernatant was completely dried *in vacuo*, and the residue was diluted with 15 mL of THF/hexane (1 : 1, *V* : *V*). Placing the mixture solution at room temperature for a week yielded orange-red needle crystals of **2** (1.7 g, 46%). m.p. 221–224 °C; ¹H NMR (C₆D₆, 400 MHz) δ : 7.39–6.39 (m), 5.95 (br), 3.20–2.89 (s, br), 2.24 (s), 1.76, 1.64, 1.21, 1.16 (s), –2.50 (br); IR (KBr) ν : 3422, 2963, 2866, 1628, 1539, 1485, 1396, 1327, 1277, 1172, 1046, 895, 783, 679 cm^{–1}. Anal. calcd for C₄₀H₅₇Cl₃LiN₂O₂Yb: C 54.33, H 6.51, N 3.17, Yb 19.57; found C 53.70, H 6.67, N 3.13, Yb 19.31.

X-ray crystal structure determination

Suitable single crystals of complexes **1** and **2** were sealed in thin-walled glass capillaries for single-crystal structure determination. Intensity data for **1** were collected at ambient temperature on a Siemens P4 four-circle diffractometer, data for **2** were collected at low temperature on Rigaku Mercury CCD with graphite monochromated Mo K α radiation. Crystal data, data collection and refinement parameters are summarized in Table 3.

Table 3 Crystallographic and refinement data for complexes **1** and **2**

	1	2
Empirical formula	C ₃₁ H ₄₄ Cl ₃ N ₂ O ₂ Yb	C ₄₀ H ₅₇ Cl ₃ LiN ₂ O ₂ Yb
Formula weight	756.07	884.24
Temperature/K	293(2)	223(1)
λ /nm	0.071073	0.071070
Crystal color and habit	Red, prism	Orange, platelet
Crystal demensions/mm ³	0.46×0.34×0.28	0.45×0.40×0.16
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> /nm	0.9023(2)	1.1467(2)
<i>b</i> /nm	2.5132(4)	2.2499(4)
<i>c</i> /nm	1.4682(3)	1.7888(3)
β (°)	96.90(1)	113.291(3)
<i>V</i> /nm ³	3.3053(11)	4.2387(13)
<i>Z</i>	4	4
<i>D</i> _{calcd} /(Mg · m ^{–3})	1.519	1.386
<i>F</i> (000)	1524	1804
μ /mm ^{–1}	3.101	2.428
Limiting indices	0 ≤ <i>h</i> ≤ 10 0 ≤ <i>k</i> ≤ 29 –17 ≤ <i>l</i> ≤ 17	–12 ≤ <i>h</i> ≤ 14 –29 ≤ <i>k</i> ≤ 29 –23 ≤ <i>l</i> ≤ 22

Continued

2 θ _{max} (°)	49.98	55.0
Reflections collected	6494	46557
Independent reflections	5732 [<i>R</i> (int)=0.0183]	9687 [<i>R</i> (int)=0.049]
Goodness-of-fit	0.899	1.02
<i>R</i>	0.0280	0.0410
<i>wR</i>	0.0470	0.1180

The crystal structures of both complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. In complex **1**, the two coordinated THF molecules are disordered, due to the strong thermal motion. Each disordered THF molecule is shown in two possible orientations.

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