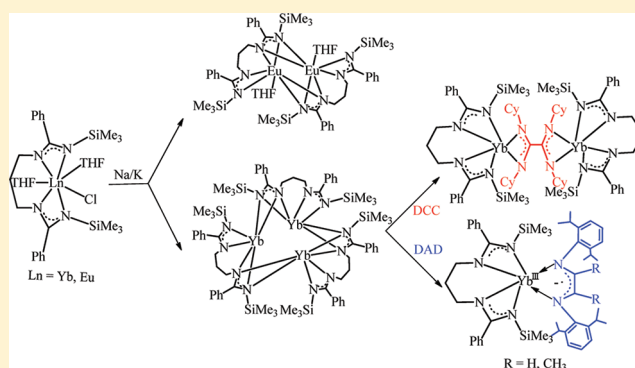


Divalent Lanthanide Complexes Supported by the Bridged Bis(amidinates) L [$L = \text{Me}_3\text{SiN}(\text{Ph})\text{CN}(\text{CH}_2)_3\text{NC}(\text{Ph})\text{NSiMe}_3$]: Synthesis, Molecular Structures and One-Electron-Transfer ReactionsLijuan Yan,[†] Haidong Liu,[†] Junfeng Wang,[†] Yong Zhang,[†] and Qi Shen^{*,†,‡}[†]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

S Supporting Information

ABSTRACT: Metathesis reactions of YbI_2 with Li_2L ($L = \text{Me}_3\text{SiN}(\text{Ph})\text{CN}(\text{CH}_2)_3\text{NC}(\text{Ph})\text{NSiMe}_3$) in THF at a molar ratio of 1:1 and 1:2 both afforded the Yb(II) iodide complex $[\{\text{YbI}(\text{DME})_2\}_2(\mu_2\text{-L})]$ (**1**), which was structurally characterized to be a dinuclear Yb(II) complex with a bridged L ligand. Treatment of EuI_2 with Li_2L did not afford the analogous $[\{\text{EuI}(\text{DME})_2\}_2(\mu_2\text{-L})]$, or another isolable Eu(II) complex, but the hexanuclear heterobimetallic cluster $[\{\text{Li}(\text{DME})_3\}^+]_2[\{(\text{EuI})_2(\mu_2\text{-I})_2(\mu_3\text{-L})_2(\text{Li})_4\}(\mu_6\text{-O})]^{2-}$ (**2**) was isolated as a byproduct in a trace yield. The rational synthesis of cluster **2** could be realized by the reaction of EuI_2 with Li_2L and H_2O in a molar ratio of 1:1.5:0.5. The reduction reaction of $\text{LLnCl}(\text{THF})_2$ ($\text{Ln} = \text{Yb}$ and Eu) with Na/K alloy in THF gave the corresponding Ln(II) complexes $[\text{Yb}_3(\mu_2\text{-L})_3]$ (**3**) and $[\text{Eu}(\mu_2\text{-L})(\text{THF})]_2$ (**4**) in good yields. An X-ray crystal structure analysis revealed that each L in complex **3** might adopt a chelating ligand bonding to one Yb atom and each Yb atom coordinates to an additional amidinate group of the other L and acts as a bridging link to assemble a macrocyclic structure. Complex **4** is a dimer in which the two monomers $[\text{Eu}(\mu_2\text{-L})(\text{THF})]$ are connected by two μ_2 -amidinate groups from the two L ligands. Complex **3** reacted with $\text{CyN}=\text{C}=\text{NCy}$ and diazabutadienes $[2,6\text{-Pr}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{R})\text{C}(\text{R})=\text{NC}_6\text{H}_3\text{Pr}_2]$ ($\text{R} = \text{H}, \text{CH}_3$) (DAD) as a one-electron reducing agent to afford the corresponding Yb(III) derivatives: the complex with an oxalamidinate ligand $[\text{LYb}\{(\text{NCy})_2\text{CC}(\text{NCy})_2\}\text{YbL}]$ (**5**) and the complexes containing a diazabutadiene radical anion $[\text{LYb}(\text{Pr}_2\text{C}_6\text{H}_3\text{NCR}(\text{R})\text{C}(\text{R})\text{NC}_6\text{H}_3\text{Pr}_2)]$ ($\text{R} = \text{H}$ (**6**), $\text{R} = \text{CH}_3$ (**7**)). Complexes **5**–**7** were confirmed by an X-ray structure determination.



■ INTRODUCTION

Divalent lanthanide (Ln(II)) complexes are efficient one-electronic transfer agents and have been widely used as reagents or precatalysts in various transformations including organic synthesis and polymerization reactions.¹ The utility of substituted cyclopentadienyl-based ligand systems has resulted in great progress in the organometallic chemistry of Ln(II).² Recently, considerable attention has been turned to the development of Ln(II) complexes supported by noncyclopentadienyl ligands, as the ligands around the central Ln(II) metals take an important rule in determining the stability and reactivity of Ln(II) complexes and noncyclopentadienyl ligands are electronic and steric tunable.³

Bridged bis(amidinates), as one of the important noncyclopentadienyl species, have found wide utility as spectator ligands in organolanthanide(III) chemistry due to the advantages of ease of access, flexibility in electronic and steric demands, limiting ligand mobility, and diverse coordination modes.^{4–6} However, the application of these ligands in the

chemistry of Ln(II) complexes is quite limited. To date, only one complex of Sm(II) with the ligand $(\text{Me}_2\text{Si}\{\text{NC}(\text{Ph})\text{N}(2,6\text{-Pr}_2\text{Ph})\}_2)$, $(\text{Me}_2\text{Si}\{\text{NC}(\text{Ph})\text{N}(2,6\text{-Pr}_2\text{Ph})\}_2)\text{SmI}_2\text{Li}_2(\text{THF})(\text{Et}_2\text{O})_2$, was synthesized and structurally characterized.⁷ To address the potential of these ligands in the Ln(II) complexes' chemistry, we are interested in the synthesis of Ln(II) complexes stabilized by these ligands and investigating the effect of these Ln(II) complexes' architectures on one-electron reductivity. For this purpose, we have designed and synthesized new Yb(II) and Eu(II) complexes bearing bridged bis(amidinates) ligand L ($L = \text{Me}_3\text{SiN}(\text{Ph})\text{CN}(\text{CH}_2)_3\text{NC}(\text{Ph})\text{NSiMe}_3$), including $[\{\text{YbI}(\text{DME})_2\}_2(\mu_2\text{-L})]$ (**1**), $[\{\text{Li}(\text{DME})_3\}^+]_2[\{(\text{EuI})_2(\mu_2\text{-I})_2(\mu_3\text{-L})_2(\text{Li})_4\}(\mu_6\text{-O})]^{2-}$ (**2**), $[\text{Yb}_3(\mu_2\text{-L})_3]$ (**3**), and $[\text{Eu}(\mu_2\text{-L})(\text{THF})]_2$ (**4**) and examined the reactivity of complex **3** as a one-electron reducing agent toward *N,N'*-dicyclohexylcarbodiimide ($\text{CyN}=\text{C}=\text{NCy}$) and

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Table 1. Crystallographic Data for Complexes 1, 2, and 4–7

	1	2	4	5	6	7
formula	C ₃₉ H ₇₄ I ₂ N ₄ O ₈ Si ₂ Yb ₂	C ₈₄ H ₁₄₄ N ₈ O ₁₃ Si ₄ I ₄ Li ₆ Eu ₂	C ₅₄ H ₈₄ N ₈ O ₂ Si ₄ Eu ₂	C ₇₂ H ₁₁₂ N ₁₂ Si ₄ Yb ₂	C ₄₉ H ₇₀ N ₆ Si ₂ Yb	C ₅₁ H ₇₄ N ₆ Si ₂ Yb
mol wt	1383.08	2439.59	1293.57	1604.18	972.33	1000.38
temp (K)	213(2)	223(2)	223(2)	223(2)	223(2)	223(2)
λ (Å)	0.71070	0.71075	0.71075	0.71075	0.71075	0.71075
cryst syst	triclinic	monoclinic	orthorhombic	triclinic	triclinic	orthorhombic
space group	P $\bar{1}$	P2 ₁ /n	Pna2 ₁	P $\bar{1}$	P $\bar{1}$	P2 ₁ 2 ₁ 2 ₁
cryst size (mm)	0.30 × 0.20 × 0.15	0.60 × 0.30 × 0.30	0.40 × 0.10 × 0.08	0.40 × 0.20 × 0.15	0.50 × 0.35 × 0.20	0.25 × 0.20 × 0.20
<i>a</i> (Å)	12.8509(12)	13.754(3)	21.584(2)	12.2179(17)	11.5883(3)	12.8252(13)
<i>b</i> (Å)	14.1330(17)	28.613(5)	10.4967(10)	17.655(3)	12.6874(5)	20.067(2)
<i>c</i> (Å)	16.3133(19)	14.661(3)	27.416(3)	19.573(3)	19.0900(9)	20.247(2)
α (deg)	85.840(9)	90	90	100.466(3)	83.044(4)	90
β (deg)	70.978(6)	104.944(3)	90	96.474(3)	77.366(4)	90
γ (deg)	79.046(8)	90	90	101.437(4)	67.269(3)	90
<i>V</i> (Å ³)	2749.8(5)	5574.6(18)	6211.3(11)	4020.5(10)	2523.95(17)	5210.8(10)
<i>Z</i> (Å ³), <i>D</i> _{calcd} (g/mL)	2, 1.670	2, 1.453	4, 1.383	2, 1.325	2, 1.279	4, 1.275
μ (mm ^{−1})	4.590	2.318	2.121	2.416	1.937	1.878
<i>F</i> (000)	1348	2440	2648	1648	1008	2080
θ range (deg)	3.01–25.35	3.07–25.50	3.09–25.50	3.18–25.50	3.05–25.50	3.18–25.50
total no. of reflns	27195	39587	21771	33088	20639	16467
no. of indep reflns	10002	10329	9403	14885	9326	9128
<i>R</i> _{int}	0.0680	0.0577	0.0876	0.0974	0.0388	0.0876
GOF	1.117	1.196	1.111	1.167	1.047	1.136
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0668	0.0759	0.0729	0.1038	0.0368	0.0904
<i>wR</i>	0.1347	0.1773	0.1160	0.1295	0.0699	0.1433
largest diff. peak and hole (e Å ^{−3})	1.320, −1.769	1.230, −1.078	0.662, −1.133	0.933, −1.105	0.689, −1.002	1.750, −1.183

diazabutadienes, [2,6-ⁱPr₂C₆H₃N=CRCR=NC₆H₃ⁱPr₂-2,6] (R=H, CH₃). Details of the synthesis and structures of complexes 1–4 and the transformations of complex 3 with CyN=C=NCy and [2,6-ⁱPr₂C₆H₃N=CRCR=NC₆H₃ⁱPr₂-2,6] leading to the corresponding Yb(III) complex with an oxalamidinate ligand, [LYb{(NCy)₂CC(NCy)₂}YbL] (5), and the Yb(III) complex with a radical anion (ⁱPr₂C₆H₃NCRCRNC₆H₃ⁱPr₂), [LYb(ⁱPr₂C₆H₃NCRCRNC₆H₃ⁱPr₂)] (R = H (6) and Me (7)), are reported here. The molecular structures of complexes 5–7 are also included.

EXPERIMENTAL SECTION

General Procedures. All manipulations and reactions were conducted under a purified argon atmosphere using standard Schlenk or glovebox techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. *N,N'*-dicyclohexylcarbodiimide (CyN=C=NCy) was purchased from Alfa Aesar and dried over CaH₂ for 48 h and distilled under reduced pressure. Li₂L [L = Me₃SiN(Ph)CN(CH₂)₃NC(Ph)NSiMe₃],⁴ LYbCl(THF)₂,⁸ and 1,4-diazabutadienes [2,6-ⁱPr₂C₆H₃N=CRCR=NC₆H₃ⁱPr₂-2,6]⁹ (R = H, CH₃) were prepared according to the literature procedures. The IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. Carbon, hydrogen, and nitrogen analyses were measured by a direct combustion using a Carlo-Erba EA 1110 instrument. ¹H NMR spectra were measured in C₆D₆ on a Unity Inova-400 instrument. The magnetic measurements were carried out on BH-55 vibrating sample magnetometer (VSM) in the magnetic field of −10 kOe to +10 kOe at room temperature under an argon atmosphere.

[{Yb(DME)₂}(μ₂-L)] (1). Into a THF solution of freshly prepared Li₂L (20 mL, 1.0 mmol) was added a THF solution of YbI₂ (40 mL, 2 mmol) under stirring at room temperature. The mixture was stirred for 24 h, and then the solvent was removed to dry under vacuum conditions. The residue was extracted with DME. The DME solution

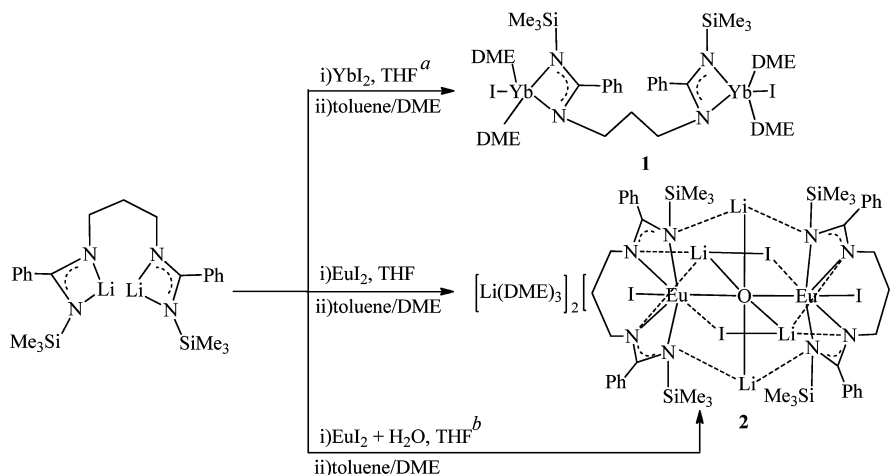
was crystallized at 0 °C to afford the crystals of NaI first. Removing the NaI by centrifugation and evaporating the solvent led to the red precipitate. The precipitate was extracted with toluene and the unsolvated part was removed. After concentration of the red solution and crystallization at 0 °C, the red crystals of complex 1 were obtained over several days (0.71 g, 51%). Anal. Calcd for C₃₉H₇₄I₂N₄O₈Yb₂: C, 33.87; H, 5.39; N, 4.05%. Found: C, 34.25; H, 5.52; N, 3.86%. ¹H NMR (400 MHz, C₆D₆): δ 7.45 (s, 3H, Ph), 7.11–7.15 (br, 4H, Ph), 7.09 (s, 3H, Ph), 3.25 (br, 12H, OCH₂CH₂O), 3.21 (br, 18H, CH₃O), 3.10 (br, 2H, NCHH), 2.10 (s, 2H, NCHH), 1.78 (s, 1H CHH), 1.40 (s, 1H CHH), 0.20–0.27 (br, 18H, SiMe₃). IR (KBr, cm^{−1}): 2958 (w), 1627 (s), 1575 (m), 1494 (w), 1447 (w), 1385 (s), 1253 (m), 1057 (m), 891 (w), 844 (m), 782 (w), 702 (m).

[{Li(DME)₃}₂]{(EuL)₂(μ₂-L)₂(μ₃-L)₂(Li)₄}(μ₆-O)}^{2−} (2). The synthesis of cluster 2 was carried out as described for complex 1, but EuI₂ (4 mL, 2 mmol) was used. Yellow crystals of cluster 2 were isolated as a byproduct in a trace yield.

A Rational Synthesis of Cluster 2. Into a solution of THF containing H₂O (40 mL, 0.5 mmol) was slowly added a THF solution of freshly prepared Li₂L (60 mL, 1.5 mmol) at −10 °C by stirring, then the solution was warmed to room temperature and stirred for 12 h. The above solution was added to a THF solution of EuI₂ (2 mL, 1 mmol) at room temperature and stirred for 12 h. The solvent was evaporated to dryness and extracted with a mixture of toluene/DME. After centrifugation to remove the precipitates, the solution was concentrated and crystallized at 0 °C. Yellow crystals of cluster 2 were obtained in 40% yield (0.49 g). Anal. Calcd for C₈₄H₁₄₄N₈O₁₃Si₄I₄Li₆Eu₂: C, 41.35; H, 5.95; N, 4.59%. Found: C, 41.04; H, 5.32; N, 4.07%. IR (KBr, cm^{−1}): 2953 (m), 2863 (m), 1604 (m), 1467 (s), 437 (s), 1412 (m), 1387 (m), 1361 (m), 1303 (s), 1239 (s), 1233 (m), 1197 (m), 1165 (m), 1130 (m), 1085 (m), 879 (s), 835 (s), 743 (m).

[Yb₃(μ₂-L)₃] (3). Into a solution of Na/K alloy (0.071 g, 2.90 mmol) in toluene (10 mL) was added a solution of LYbCl(THF)₂ (1.88 g, 2.42 mmol) in THF (30 mL). The reaction mixture was stirred for 48 h at room temperature. The solvent was evaporated in a

Scheme 1.



^aMolar ratio of 1:1 or 1:2. ^bMolar ratio of 1.5:1:0.5.

vacuum to dryness and extracted with toluene (2 × 15 mL) followed by centrifugation to remove the NaCl. The volume of the extract was reduced to 0.5 mL; then hexane (6 mL) was added. Cooling the solution to 0 °C afforded complex 3 as black crystals (0.87 g, 60%). Anal. Calcd for C₆₉H₁₀₂N₁₂Si₆Yb₃: C, 46.37; H, 5.75; N, 9.40%. Found: C, 46.77; H, 6.15; N, 9.16%. ¹H NMR (400 MHz, C₆D₆): δ 7.30–6.91 (br, 30H, Ph), 3.77 (br, 6H, NCHH), 3.24 (s, 6H, NCHH), 2.06 (s, 6H, CH₂), 1.18–0.84 (m, 54H, SiMe₃). IR (KBr, cm⁻¹): 2952 (s), 2361 (m), 1647 (m), 1601 (s), 1569 (s), 1541 (s), 1448 (s), 1384 (s), 1250 (s), 1201 (m), 1156 (w), 1074 (w), 970 (m), 902 (m), 836 (s), 780 (m), 748 (m), 700 (s).

[Eu(μ₂-L)(THF)]₂ (4). Into a THF solution of freshly prepared Li₂L (80 mL, 2.4 mmol) was added a suspension of EuCl₃ (0.62 g, 2.4 mmol) in THF (40 mL) with stirring at room temperature for 24 h. Into a solution of Na/K alloy (0.071 g, 2.88 mmol) in toluene (10 mL) was added the above suspension. The mixture was stirred for three days. The solvent was evaporated in a vacuum to dryness and extracted with toluene followed by centrifugation to remove the NaCl. The solution was concentrated and crystallized at room temperature for one day. Complex 4 was isolated as yellow crystals (1.0 g, 60%). Anal. Calcd for C₅₄H₈₄N₈O₂Si₄Eu₂: C, 49.95; H, 6.84; N, 8.64%. Found: C, 49.35; H, 6.45; N, 8.55%. IR (KBr, cm⁻¹): 2953 (s), 2901 (m), 1614 (s), 1470 (s), 1303 (s), 1236 (s), 1200 (w), 1165 (w), 1133 (w), 1002 (w), 877 (m), 832 (m), 745 (w).

LYb{(NCy)₂CC(NCy)₂}YbL (5). Into a solution of CyN=C=NCy (0.37 g, 1.80 mmol) in toluene (20 mL) was slowly added a solution of complex 3 (1.07 g, 0.6 mmol) in toluene (30 mL). The color of the solution changed immediately from black to yellow. The reaction mixture was stirred for another 12 h at room temperature. The solvent was evaporated in a vacuum to dryness and extracted with DME (8 mL). Colorless crystals of complex 5 were obtained (0.56 g, 39%) at room temperature. Anal. Calcd for C₇₂H₁₁₂N₁₂Si₄Yb₂ (1604.18): C, 53.91; H, 7.04; N, 10.48%. Found: C, 53.70; H, 7.18; N, 10.08%. IR (KBr, cm⁻¹): 2928 (s), 2852 (m), 2363 (w), 1647 (s), 1618 (s), 1448 (m), 1365 (m), 1240 (s), 1154 (w), 1072 (w), 1001 (m), 901 (w), 832 (s), 745 (w), 699 (s).

LYb{Pr₂C₆H₃NCHCHNC₆H₃Pr₂} (6). Into a solution of [2,6-Pr₂C₆H₃N=CHCH=NC₆H₃Pr₂-2,6] (0.87 g, 2.31 mmol) in toluene (20 mL) was slowly added a solution of complex 3 (1.37 g, 0.77 mmol) in toluene (40 mL). The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated in a vacuum to dryness and extracted with Et₂O (5 mL). Green crystals of complex 6 were obtained (0.90 g, 40%) at room temperature. Anal. Calcd for C₄₉H₇₀N₆Si₂Yb (972.33): C, 60.53; H, 7.26; N, 8.64%. Found: C, 59.76; H, 7.25; N, 8.30%. IR (KBr, cm⁻¹): 2962 (s), 2869 (w), 2363 (m), 2345 (w), 1627 (s), 1566 (w), 1466 (m), 1384 (s), 1253 (m), 1177 (w), 1107 (w), 1047 (w), 923 (w), 837 (m), 761 (m), 700 (m).

LYb{Pr₂C₆H₃NC(Me)C(Me)NC₆H₃Pr₂} (7). The synthesis of complex 7 was carried out as described for complex 6, but [2,6-Pr₂C₆H₃N=C(Me)C(Me)=NC₆H₃Pr₂-2,6] (0.88 g, 2.16 mmol) and complex 3 (1.28 g, 0.72 mmol) were used. Orange crystals of complex 7 were obtained from a Et₂O solution (0.91 g, 42%) at room temperature. Anal. Calcd for C₅₁H₇₄N₆Si₂Yb (1000.33): C, 61.23; H, 7.46; N, 8.40%. Found: C, 61.02; H, 7.56; N, 8.16%. IR (KBr, cm⁻¹): 2962 (s), 2869 (m), 1642 (s), 1464 (m), 1435 (m), 1363 (s), 1241 (m), 1184 (m), 1120 (m), 933 (w), 831 (m), 762 (s), 700 (s).

X-Ray Crystallography. Crystals of complexes 1–7 suitable for X-ray diffraction were sealed in a thin-walled glass capillary filled under argon. Diffraction data were collected on a Rigaku Mercury CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71070 Å) for complex 1 and on a Rigaku Saturn CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71075 Å) for complexes 2–7. 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 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on |F|². All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 programs.

RESULTS AND DISCUSSION

1. Reaction of YbI₂ with Li₂L: Synthesis and Molecular Structure of [{YbI(DME)}₂(μ₂-L)] (1) (L = Me₃SiN(Ph)CN(CH₂)₃NC(Ph)NSiMe₃). The metathesis reaction of LnI₂ with alkali metal salt is a general route for the synthesis of Ln(II) complexes. Thus, the reaction of YbI₂ with freshly prepared Li₂L in a molar ratio of 1:1 was tried at room temperature for 24 h. After workup, red crystals were isolated upon crystallization from a toluene solution at 0 °C in 21% yield. Elemental analysis results of the red crystals are not consistent with the formula of the expected complex LYb(DME) but are in accordance with those of the moniodide complex [{YbI(DME)}₂(μ₂-L)] (1) (Scheme 1). ¹H NMR spectra of complex 1 in C₆D₆ indicated the existence of L and DME. The identity of complex 1 was established by an X-ray crystal structure analysis.

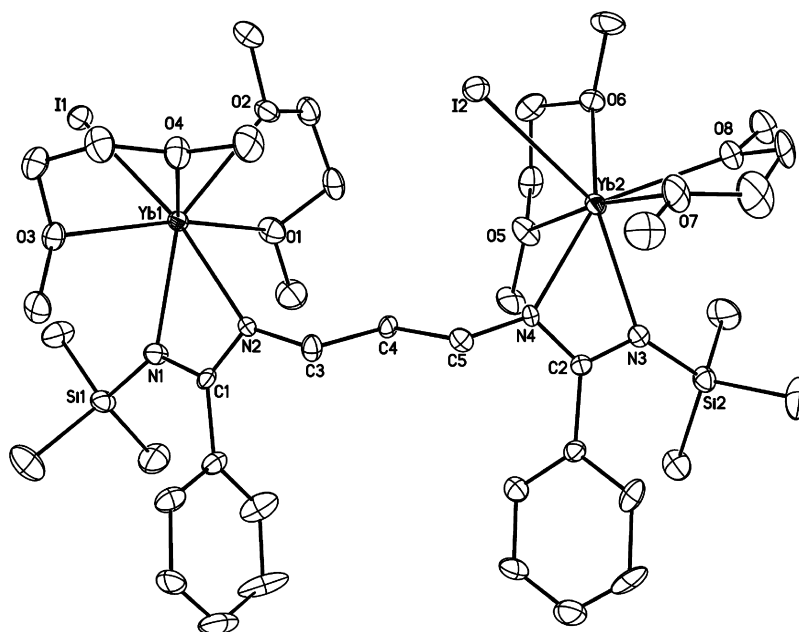


Figure 1. Molecular structure of complex **1**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **1** and **2**

1			
Yb(1)–N(1)	2.461(8)	Yb(2)–N(3)	2.457(8)
Yb(1)–N(2)	2.433(8)	Yb(2)–N(4)	2.440(8)
Yb(1)–I(1)	3.1336(8)	Yb(2)–I(2)	3.1622(10)
Yb(1)–O(1)	2.514(8)	Yb(2)–O(5)	2.492(6)
Yb(1)–O(2)	2.520(7)	Yb(2)–O(6)	2.559(7)
Yb(1)–O(3)	2.512(7)	Yb(2)–O(7)	2.516(8)
Yb(1)–O(4)	2.565(7)	Yb(2)–O(8)	2.541(8)
N(2)–Yb(1)–N(1)	55.7(3)	N(4)–Yb(2)–N(3)	55.3(3)
N(2)–Yb(1)–I(1)	168.67(18)	N(3)–Yb(2)–I(2)	144.6(2)
2			
Eu(1)–O(1)	2.4526(5)	Eu(1)–N(1)	2.751(6)
Eu(1)–N(2)	2.688(7)	Eu(1)–N(3)	2.728(7)
Eu(1)–N(4)	2.724(7)	Eu(1)–I(1)	3.2406(9)
Eu(1)–I(2)	3.2602(8)	N(1)–Li(2)	2.052(15)
N(2)–Li(1)	2.127(15)	N(3)–Li(2A)	2.092(16)
N(4)–Li(1)	2.138(15)	O(1)–Eu(1)–I(1)	169.51(2)
N(1)–Eu(1)–N(2)	50.1(2)	N(3)–Eu(1)–N(4)	49.5(2)
N(2)–Eu(1)–N(4)	66.2(2)	Eu(1)–O(1)–Eu(1A)	180.000(13)
Li(1)–O(1)–Li(1A)	180.000(2)	Li(2)–O(1)–Li(2A)	180.000(3)

Thus, the low yield of complex **1** might be attributed to the shortage of the amount of YbI_2 used. Indeed, complex **1** can be prepared in 51% yield by the reaction of YbI_2 with Li_2L in a molar ratio of 2:1 (Scheme 1).

Complex **1** is very sensitive to air and moisture but thermally stable.

Bimetallic Ln(II) complexes are not many. To the best of our knowledge, this is the first example of a molecular structure of a bimetallic Yb(II) monohalide with a bridged ligand.

The molecular structure of complex **1** is shown in Figure 1, and selective bond lengths and angles are listed in Table 2. Complex **1** has a dimetallic framework with the ligand **L** in a bridging mode. Each Yb atom is ligated by one amidinate group, one iodide atom, and two DME molecules in a distorted pentagonal bipyramid. The bond parameters around the two Yb atoms are not identical, but they are equivalent within the

error limits. The average bond length of Yb–N (2.447(8) Å for Yb(1) and 2.448(8) Å for Yb(2)) and the bond angle of N–Yb–N (55.7(3)° for Yb(1) and 55.3(3)° for Yb(2)) are very comparable with those found in the Yb(II) complexes supported by two monoamidinate¹⁰ and two monoguanidinate ligands.^{3m} The bond length of Yb–I matches those of the Yb(II) iodides with terminal I.¹¹

Ln(II) halide complexes are well-known to be precursors to the corresponding Ln(II) derivatives. Thus, the reactivity of complex **1** with alkali metal salts was then investigated. Unfortunately, complex **1** did not react with either Li_2L or NaCp.

2. Reaction of EuI_2 with Li_2L to a Byproduct $[\{\text{Li}(\text{DME})_3\}^+][\{(\text{EuI})_2(\mu_2\text{-I})_2(\mu_3\text{-L})_2(\text{Li})_4(\mu_6\text{-O})\}]^{2-}$ (2**): Molecular Structure and Rational Synthesis of Complex **2**.** It is unexpected that replacing YbI_2 by EuI_2 led to the isolation of

the byproduct hexanuclear heterobimetallic cluster $[\{\text{Li}(\text{DME})_3\}^+]_2[\{(\text{EuI})_2(\mu_2\text{-I})_2(\mu_3\text{-L})_2(\text{Li})_4\}(\mu_6\text{-O})]^{2-}$ (**2**) as light yellow crystals in a trace yield (Scheme 1). Attempts to isolate the main product by treatment of the mother liquid with different solvents were unsuccessful. The magnetic moment of cluster **2** was measured, and the value equals $7.92 \mu_{\text{B}}$, which is consistent with the ground state expected for a Eu(II) (P) ion.¹² Cluster **2** was further confirmed with an X-ray diffraction study.

The formation of the byproduct of cluster **2** might be attributed to the use of a contaminated solvent or a solution of LiBu^n with a trace of H_2O . Indeed, the rational synthesis of cluster **2** could be realized by the reaction of EuI_2 with 1.5 equiv of freshly prepared Li_2L containing 0.5 equiv of water in 40% yield (Scheme 1).

The molecular structure of cluster **2** is shown in Figure 2. Selected bond lengths and angles are listed in Table 2.

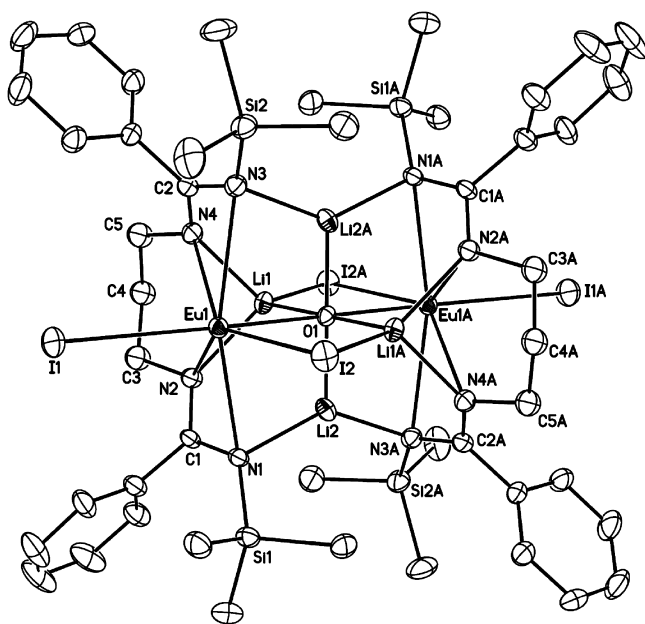


Figure 2. Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Cluster **2** is composed of discrete ion pairs: one dianion $[\{(\text{EuI})_2(\mu_2\text{-I})_2(\mu_3\text{-L})_2(\text{Li})_4\}(\mu_6\text{-O})]^{2-}$ and two cations $2[\text{Li}(\text{DME})_3]^+$. The dianion is built up by an O-centered symmetrical hexagon of $\text{Eu}_2\text{Li}_2(\text{Li}(1), \text{Li}(1\text{A}))\text{I}_2$ and a macrocycle formed by two bridged lithium atoms and two L ligands via four Eu–amidinate bonds and four Li–N bonds. The coordinate geometry around each Eu atom can be described as a distorted trigonal bipyramid, when each chelating amidinate ligand of L was considered to occupy one coordination vertex. The bond lengths of Eu–N in cluster **2** range from 2.688(7) to 2.751(6) Å with the average value of 2.723(7) Å. The value is about 0.09 Å longer than those found in the Eu(II) bis(amidinate) complex $[\text{Eu}^{\text{II}}\{\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}^i)_2\}_2(\text{THF})_2]$.¹³ This is reasonable because a bond length of a metal to a terminal ligand is usually shorter than that of a metal to a bridged ligand bond. However, the average Eu–N bond length here is about 0.20 Å longer than that found in the Eu(III) complex $\text{Li}(\text{DME})_3(\text{Eu}^{\text{III}}\text{L}_2)$,^{6b} indicative of a +2

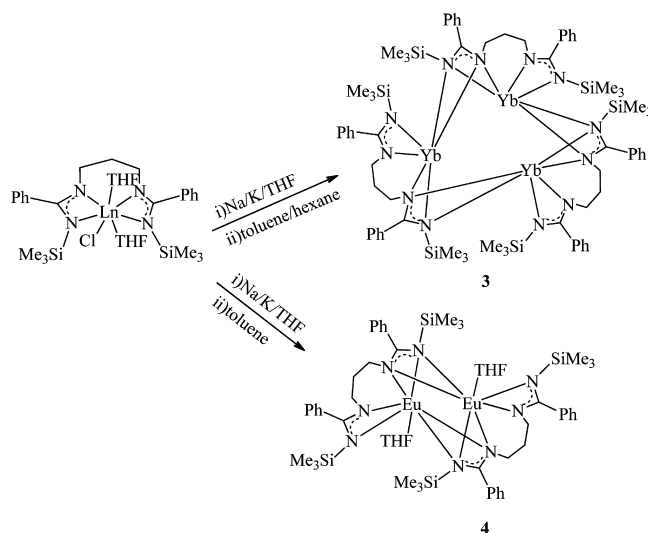
oxidation state of Eu in cluster **2**, as the difference in ion radius between Eu(III) and Eu(II) is about 0.14 Å.¹⁴

The coordination geometries around Li atoms in the dianion can be divided into two types: one is a trigon (Li(2) and Li(2A)); the other is a tetrahedron (Li(1), Li(1A)). The bond parameters around Li(2) (Li(2A)) and Li(3) (Li(3A)) are not identical, but they are equivalent within the error limits. The Li–N bond distances range from 2.052(15) to 2.138(15) Å, which are comparable to those found in lithium amidinate complexes.¹⁵

3. Reduction of $\text{LLnCl}(\text{THF})_2$ with Na/K Alloy: Synthesis and Molecular Structures of $[\text{Yb}_3(\mu_2\text{-L})_3]$ (3**) and $[\text{Eu}(\mu_2\text{-L})(\text{THF})]_2$ (**4**).** The reduction reaction of $\text{LLnCl}(\text{THF})_2$ by Na/K alloy was then studied to see whether the complex LiL could be stabilized. Treatment of $\text{LYbCl}(\text{THF})_2$ with Na/K alloy at room temperature in THF afforded the black crystals in 60% yield upon crystallization. ¹H NMR of the crystals in solution showed the complex is diamagnetic, consistent with the Yb(II) oxidation state.

A crystal structure analysis indicated that the crystals are the trinuclear macrocyclic Yb(II) complex $[\text{Yb}_3(\mu_2\text{-L})_3]$ (**3**) (Scheme 2). Although the detailed bond parameters of complex

Scheme 2



3 could not be given due to the quality of the crystals, the trinuclear macrocyclic structure skeleton of complex **3** is observed clearly (Figure 3, see Supporting Information). Each L in complex **3** might adopt a chelating ligand bonding to one Yb atom, and each Yb atom coordinates to an additional amidinate group of another L and acts as a bridging link to assemble a macrocyclic structure. The overall macrocyclic structure seems rather symmetric. A great effort to obtain the fine single crystals has not been successful yet.

Anhydrous EuCl_3 reacted with an equivalent of Li_2L in THF, followed by treatment with Na/K alloy at a molar ratio of 1:1.2 at 50 °C for three days, giving the Eu(II) complex $[\text{Eu}(\mu_2\text{-L})(\text{THF})]_2$ (**4**) as orange-red air- and moisture-sensitive crystals (Scheme 2). The IR spectrum showed the strong absorption of the C=N stretch at approximately 1640 cm^{-1} , indicative of the delocalized double bond of N=C=N linkage.^{8,16} The magnetic moment of complex **4** ($7.67 \mu_{\text{B}}$) indicates the oxidation state of Eu being +2.¹² The further confirmation of complex **4** was made by X-ray diffraction

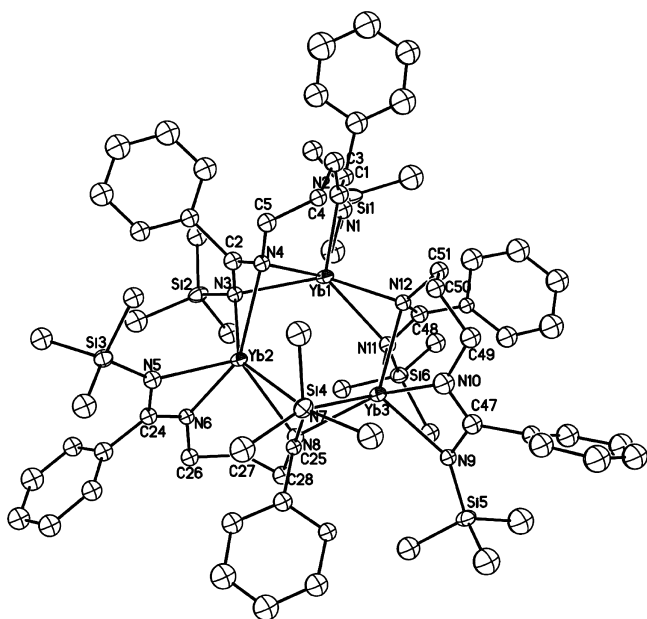


Figure 3. Molecular structure of complex 3. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

studies. The molecular structure of complex 4 is shown in Figure 4. Selected bond distances and angles are provided in Table 3.

Complex 4 is a dimer in which two monomers $[\text{Eu}(\mu_2\text{-L})(\text{THF})]$ are connected by two μ_2 -amidinate groups from the two L ligands. The coordinate geometry around each Eu atom is a distorted tetrahedron with each bidentate amidinate ligand occupying one coordination vertex. The distances from the Eu atom to the C atoms of the amidinate skeleton are 3.040(14), 2.976(15), and 2.950(11) Å for Eu(1) and 3.139(17), 3.023(12), and 2.918(17) Å for Eu(2), which are close to the values of $\text{Eu}-\eta^5\text{Cp}$ (2.765(10)–2.822(9) Å).¹⁷ Therefore, the bonding mode of each amidinate group to each Eu ion in

complex 4 is close to an η^3 fashion. The average Eu–N bond distance (2.561(12) Å) for the terminal amidinate groups can be compared with that in complex $[\text{Eu}^{\text{II}}\{\text{PhC}(\text{NSiMe}_3)(\text{NC}_6\text{H}_3\text{Pr}'_2\text{-2,6})\}_2(\text{THF})_2]$.¹³ The average bond length of Eu–N of the bridged amidinate groups (2.748(12) Å) is about 0.187 Å longer. Such a long bond distance is also found in cluster 2 (2.723(7) Å). The bond angle of N–Eu–N in complex 4 is more acute than those found in the other Ln(II) amidinate complexes.^{10,31} This may be attributed to the steric demand in the dimer skeleton.

3. One-Electron-Transfer Reactions. *Reaction of Complex 3 with N,N' -Dicyclohexylcarbodiimide ($\text{CyN}=\text{C}=\text{NCy}$): Synthesis and Molecular Structure of $[\text{LYb}\{(\text{NCy})_2\text{CC}(\text{NCy})_2\}\text{YbL}]$ (5).* Carbodiimides are of interest for Ln(II)-based reactivity studies.^{13,18,19} We have reported that the N,N' -diamine bridged bis(phenolates) Yb(II) complex, $(\{-\text{OC}_6\text{H}_2(2,4\text{-}^t\text{Bu}_2)-(6\text{-CH}_2)_2\}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{Yb}(\text{THF})_2$, could react with N,N' -diisopropylcarbodiimide ($^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$) affording a Yb(III) complex with a diaminocarbene ligand via the reduction of a $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ by two molecules of the Yb(II) complex.¹⁹ While, the reaction of ansa-heteroborabenzene Yb(II) amide with $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ yielded a new Yb(II) complex via the insertion of $^i\text{PrN}=\text{C}=\text{N}^i\text{Pr}$ into the Yb–N bond, no redox reaction occurred.^{3k}

To assess the one electron transfer reactivity of complex 3, and the influence of Yb(II) complexes on the reduction mode of carbodiimides, the reaction of complex 3 with $\text{CyN}=\text{C}=\text{NCy}$ in a molar ratio of 1:1 was investigated in toluene at room temperature. The reaction went smoothly, and the color change from black to yellow gradually, indicative of the oxidation of Yb(II), was observed. After workup, colorless crystals were obtained from a DME solution in 39% yield. The full characterization including a single crystal structural analysis indicated that the crystals are the Yb(III) complex with a newly formed oxalamidinate ligand $[\text{LYb}\{(\text{NCy})_2\text{CC}(\text{NCy})_2\}\text{YbL}]$ (5) by reductive coupling of $\text{CyN}=\text{C}=\text{NCy}$ (Scheme 3). Complex 5 represents the first example of the reduction of carbodiimides to an oxalamidinate ligand by Yb(II) complexes,

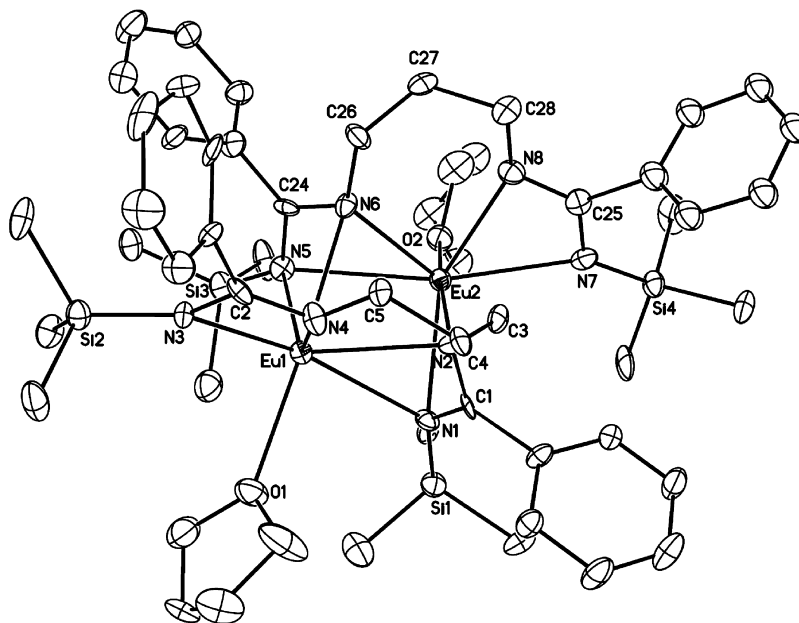


Figure 4. Molecular structure of complex 4. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 4

4			
Eu(1)–N(1)	2.845(12)	Eu(2)–N(1)	2.678(10)
Eu(1)–N(2)	2.618(12)	Eu(2)–N(2)	2.870(11)
Eu(1)–N(3)	2.629(12)	Eu(2)–N(5)	2.880(13)
Eu(1)–N(4)	2.483(11)	Eu(2)–N(6)	2.630(12)
Eu(1)–N(5)	2.700(10)	Eu(2)–N(7)	2.659(16)
Eu(1)–N(6)	2.764(12)	Eu(2)–N(8)	2.473(12)
Eu(1)–C(1)	3.040(14)	Eu(2)–C(1)	3.023(12)
Eu(1)–C(2)	2.976(15)	Eu(2)–C(25)	2.918(17)
Eu(1)–C(24)	2.950(11)	Eu(2)–C(24)	3.139(17)
Eu(1)–O(1)	2.563(10)	Eu(2)–O(2)	2.614(11)
N(1)–Eu(1)–N(2)	49.2(3)	N(1)–Eu(2)–N(2)	48.4(3)
N(3)–Eu(1)–N(4)	52.9(4)	N(7)–Eu(2)–N(8)	53.8(4)
N(5)–Eu(1)–N(6)	48.9(3)	N(5)–Eu(2)–N(6)	48.2(3)
N(2)–Eu(1)–N(4)	72.4(4)	N(8)–Eu(2)–N(6)	73.3(4)

Scheme 3

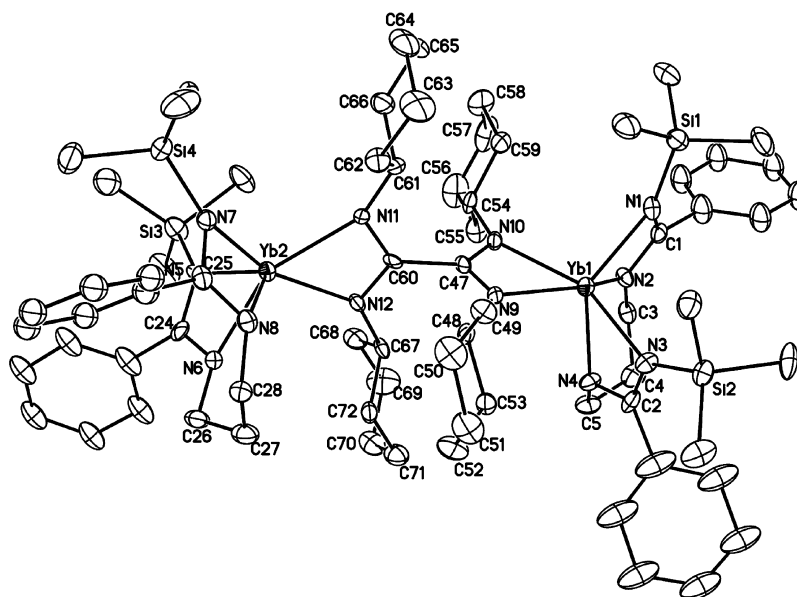
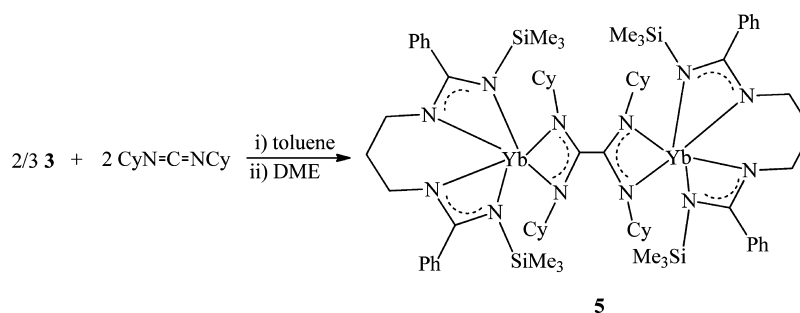


Figure 5. Molecular structure of complex 5. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Yb(1)–N(1) 2.304(10), Yb(1)–N(2) 2.281(8), Yb(1)–N(3) 2.337(9), Yb(1)–N(4) 2.249(8), Yb(1)–N(9) 2.346(9), Yb(1)–N(10) 2.300(9), Yb(2)–N(5) 2.313(10), Yb(2)–N(6) 2.288(9), Yb(2)–N(7) 2.338(9), Yb(2)–N(8) 2.279(10), Yb(2)–N(11) 2.326(9), Yb(2)–N(12) 2.328(9), N(9)–C(47) 1.299(13), N(10)–C(47) 1.313(12), C(47)–C(60) 1.520(15), N(11)–C(60) 1.339(12), N(12)–C(60) 1.325(12); N(1)–Yb(1)–N(2) 58.7(3), N(3)–Yb(1)–N(4) 58.9(3), N(9)–Yb(1)–N(10) 56.9(3), N(9)–C(47)–N(10) 115.8(10), N(11)–C(60)–N(12) 114.5(10), N(5)–Yb(2)–N(6) 59.0(3), N(7)–Yb(2)–N(8) 58.3(3), N(11)–Yb(2)–N(12) 57.5(3).

although the reduction mode here has already been found in the cases with Sm(II) complexes.^{18b–d}

The molecular structure of complex 5 was determined and is shown in Figure 5 with the selected bond distances and angles. Each Yb atom in complex 5 is bound in an amidinate style to

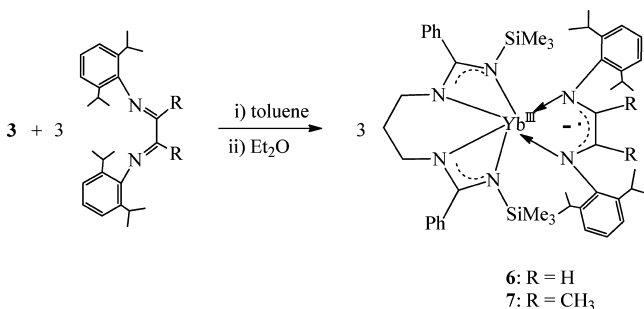
either side of a tetracyclo-hexyloxalamidinate (2-) ligand with one L ligand completing each coordination sphere. The coordinated geometry around each Yb atom can be described as a distorted tetragonal pyramid if the oxalamidinate ligand is considered to occupy one coordinate site. The solid-state

structure is similar to those of the analogous Sm(III) complexes.^{18b–d}

Reactions of Complex 3 with Diazabutadienes: Synthesis and Molecular Structures of $\text{LYb}^{\text{III}}(\text{Pr}_2\text{C}_6\text{H}_3\text{NCRNC}_6\text{H}_3^i\text{Pr}_2)$ ($R = \text{H}$ (6), CH_3 (7)). Diazabutadienes have remarkable electron affinity.²⁰ They can oxidize electropositive Ln metals by accepting one or two electrons to transfer to a radical anion²¹ or dianion.^{21b} The reactions of Yb(II) complexes supported by cyclopentadienyl (indenyl, fluorenyl) ligands with diazabutadienes are well documented.²¹ In 2008, the reactivity of Yb(II) boratabenzene complex $(\text{C}_5\text{H}_5\text{BNPh}_2)_2\text{Yb}(\text{THF})_2$ toward $\text{PhNC}(\text{Me})\text{C}(\text{Me})\text{NPh}$ was reported to give a Yb(III) complex, and the redox process was found to be solvent sensitive and reversible.²²

To further explore the chemistry of bridged bis(amidinate) Yb(II) complexes, the reactions of complex 3 with diazabutadienes $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{R})\text{C}(\text{R})=\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-}2,6]$ ($R = \text{H}$ and CH_3) were investigated. Reaction of complex 3 with an equivalent of $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CHCH}=\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-}2,6]$ in toluene at room temperature led to a red-brown solution, from which light green crystals were obtained upon crystallization from a Et_2O solution in 40% yield. The ^1H NMR spectroscopy of the crystals in C_6D_6 showed a paramagnetic property. X-ray crystal structure analyses demonstrated that the crystals are $[\text{LYb}^{\text{III}}(\text{Pr}_2\text{C}_6\text{H}_3\text{NCHCHNC}_6\text{H}_3^i\text{Pr}_2)]$ (6) with a radical anion ($^i\text{Pr}_2\text{C}_6\text{H}_3\text{NCHCHNC}_6\text{H}_3^i\text{Pr}_2$) (Scheme 4).

Scheme 4



Replacing $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CHCH}=\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-}2,6]$ with $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-}2,6]$ resulted in the formation of the analogous complex $[\text{LYb}^{\text{III}}(\text{Pr}_2\text{C}_6\text{H}_3\text{NC}(\text{Me})\text{C}(\text{Me})\text{NC}_6\text{H}_3^i\text{Pr}_2)]$ (7), as orange crystals in 42% yield (Scheme 4). Complex 7 also shows a paramagnetic property in C_6D_6 . The identity of complex 7 was established by an X-ray structure determination.

Complexes 6 and 7 are highly air- and moisture-sensitive but thermally stable. They are soluble in THF and Et_2O and sparingly soluble in hexane.

The molecular structures of complexes 6 and 7 are shown in Figures 6 and 7 with selective bond lengths and bond angles, respectively.

The molecular structures of complexes 6 and 7 are quite similar. Each Yb center adopts a distorted octahedral geometry around two amidinate groups of L and one diazabutadiene ligand bound through two N atoms. The bond lengths of Yb–N of amidinate groups (ranging from 2.304(3) to 2.328(3) Å for complex 6 and 2.308(10) to 2.332(11) Å for complex 7) are about 0.13–0.15 Å shorter than those in complex 1 (2.461(8), 2.440(8), 2.433(8), and 2.457(8) Å) and in $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{Yb}(\text{THF})_2$ (2.468(2) and 2.478(2)),¹⁰ which are

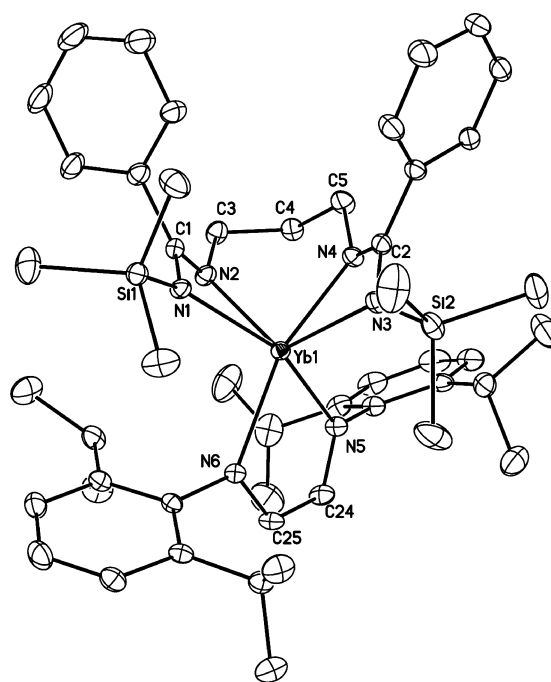


Figure 6. Molecular structure of complex 6. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)–N(1) 2.328(3), Yb(1)–N(2) 2.310(3), Yb(1)–N(3) 2.320(3), Yb(1)–N(4) 2.304(3), Yb(1)–N(5) 2.365(3), Yb(1)–N(6) 2.379(3), N(5)–C(24) 1.329(5), N(6)–C(25) 1.335(4), C(24)–C(25) 1.396(5); N(1)–Yb(1)–N(2) 58.53(10), N(3)–Yb(1)–N(4) 58.36(10), N(5)–Yb(1)–N(6) 70.40(10).

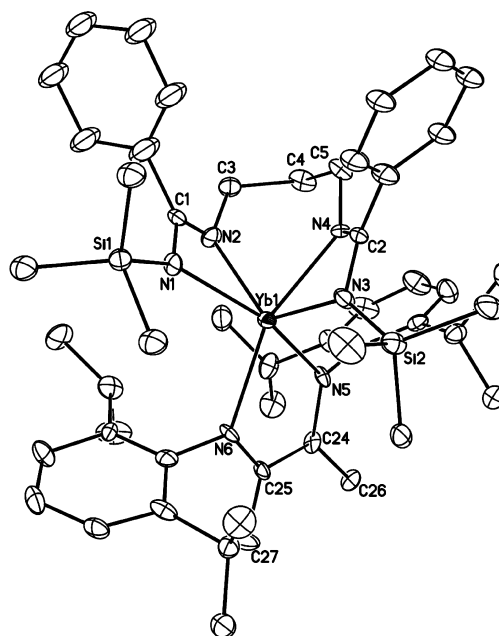


Figure 7. Molecular structure of complex 7. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)–N(1) 2.332(11), Yb(1)–N(2) 2.317(11), Yb(1)–N(3) 2.308(10), Yb(1)–N(4) 2.313(10), Yb(1)–N(5) 2.328(10), Yb(1)–N(6) 2.394(9), N(5)–C(24) 1.385(17), N(6)–C(25) 1.348(15), C(24)–C(25) 1.395(18); N(1)–Yb(1)–N(2) 57.5(4), N(3)–Yb(1)–N(4) 58.8(4), N(5)–Yb(1)–N(6) 69.5(3).

in agreement with the ionic radii difference between Yb(II) and Yb(III) (0.155 Å),^{21b} indicative of oxidation of Yb(II) in complex 3.

The two almost equal Yb–N bond lengths (in error limits, 2.365(3) and 2.379(3) Å in complex 6; and 2.328(10) and 2.313(10) Å in complex 7) and a delocalized NCCN π system (N=C bonds, 1.329(5) and 1.335(4) Å in complex 6 and 1.385(17) and 1.348(15) Å in complex 7; C–C bond, 1.396(5) Å in complex 6 and 1.395(18) Å in complex 7) were observed in the YbDAD part of both complexes. The coordination pattern of the DAD ligand to a Yb ion here is usual in the systems with Cp complexes.^{21a–d}

The geometry parameters of complexes 6 and 7 indicate unequivocally reduced radical-anionic character of the diazabutadiene ligands and the 3+ oxidation state of Yb metal in both complexes.

The well-known bond valence sum (BVS) could be used as a convenient method to estimate the oxidation state of a central metal in a complex.²³ To further confirm the central metal Yb in complexes 6 and 7 being in the +3 oxidation state, the BVS calculation for both complexes was made. Indeed, the values are equal to 3.37 for complex 6 and 3.39 for complex 7.

CONCLUSION

In summary, four kinds of Ln(II) complexes supported by bridged bis(amidinate) ligand L, [$\{Yb(DME)_2\}_2(\mu_2-L)$] (1), [$\{Li(DME)_3\}^+_2\{EuI_2(\mu_2-I)_2(\mu_3-L)_2(Li)_4\}(\mu_6-O)\}^{2-}$] (2), [$Yb_3(\mu_2-L)_3$] (3) and [$Eu(\mu_2-L)(THF)_2$] (4), were synthesized and structurally characterized. Complex 3 can serve as a one-electron reducing agent to reduce CyN=C=NCy and diazabutadienes, [$2,6-iPr_2C_6H_3N=CRCR=NC_6H_3^iPr_2-2,6$] (R = H, Me), respectively, with the formation of Yb(III) complex bearing an oxalamidinate ligand [$LYb\{N(Cy)_2CC(NCy)_2\}YbL$] (5) and the Yb(III) complexes with a diazabutadiene radical anion [$LYb-(^iPr_2C_6H_3NCRCRNC_6H_3^iPr_2)$] (R = H (6), CH₃ (7)).

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data of complexes 1–7 are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, 102, 2693. (b) Kagan, H. B. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fraga, I. L., Eds.; Reidel: Dordrecht, The Netherlands, 1985; p 49. (c) Collin, J.; Giuseppone, N.; Van de Weghe, P. *Coord. Chem. Rev.* **1998**, 117, 178. (d) Hou, Z.-M.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, 231, 1. (e) Edmonds, D. J.; Johnston, D.; Procter, D. J. *Chem. Rev.* **2004**, 104, 3371. (f) Gromada, J.; Carpentier, J.-F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, 248, 397.

- (2) (a) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, 102, 2119. (b) Evans, W. J. *J. Organomet. Chem.* **2002**, 647, 2. (c) Evans, W. J. *Coord. Chem. Rev.* **2000**, 206–207, 263. (d) Hou, Z.-M.; Yoda, C.; Koizumi, T.-a.; Nishiura, M.; Wakatsuki, Y.; Fukuzawa, S.-i.; Takats, J. *Organometallics* **2003**, 22, 3586. (e) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, 102, 1953. (f) Hou, Z.-M.; Wakatsuki, Y. *J. Organomet. Chem.* **2002**, 647, 61. (g) Kirillov, E.; Saillard, J.-Y.; Carpentier, J.-F. *Coord. Chem. Rev.* **2005**, 249, 1221. (h) Bochkarev, M. N. *Coord. Chem. Rev.* **2004**, 248, 835.
- (3) (a) Hou, Z.-M.; Koizumi, T.-a.; Nishiura, M.; Wakatsuki, Y. *Organometallics* **2001**, 20, 3323. (b) Deng, M. Y.; Yao, Y. M.; Shen, Q.; Zhang, Y.; Sun, J. *Dalton Trans.* **2004**, 944. (c) Deacon, G. B.; Fanwick, P. E.; Gitlits, A.; Rothwell, I. P.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2001**, 1505. (d) Zhou, H.; Guo, H. D.; Yao, Y. M.; Zhou, L. Y.; Sun, H. M.; Sheng, H. T.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2007**, 46, 958. (e) Hou, Z.-M.; Zhang, Y.; Nishiura, M.; Wakatsuki, Y. *Organometallics* **2003**, 22, 129. (f) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2005**, 690, 5078. (g) Guo, H. D.; Zhou, H.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2007**, 3555. (h) Dugah, D. T.; Skelton, B. W.; Delbridge, E. E. *Dalton Trans.* **2009**, 1436. (i) Zhou, L.; Wang, J.; Zhang, Y.; Yao, Y.; Shen, Q. *Inorg. Chem.* **2007**, 46, 5763. (j) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, 102, 1851. (k) Cui, P.; Chen, Y.; Li, G.; Xia, W. *Angew. Chem., Int. Ed.* **2008**, 47, 9944. (l) Cole, M. L.; Junk, P. C. *Chem. Commun.* **2005**, 2695. (m) Heitmann, D.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Dalton Trans.* **2007**, 187.
- (4) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, 20, 782.
- (5) (a) Wang, J.; Cai, T.; Yao, Y.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2007**, 5275. (b) Wang, J.; Yao, Y.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2009**, 48, 744. (c) Wang, J.; Sun, H.; Yao, Y.; Zhang, Y.; Shen, Q. *Polyhedron* **2008**, 27, 1977.
- (6) (a) Wang, J.; Xu, F.; Cai, T.; Shen, Q. *Org. Lett.* **2008**, 10, 445. (b) Wang, J.; Li, J.; Xu, F.; Shen, Q. *Adv. Synth. Catal.* **2009**, 351, 1363.
- (7) Pan, C. L.; Chen, W.; Song, S.; Zhang, H.; Li, X. *Inorg. Chem.* **2009**, 48, 6344.
- (8) Wang, J.; Yao, Y.; Cheng, J.; Pang, X. A.; Zhang, Y.; Shen, Q. *J. Mol. Struct.* **2005**, 743, 229.
- (9) Türkmen, H.; Çetinkaya, B. *J. Organomet. Chem.* **2006**, 691, 3749.
- (10) Wedler, M.; Noltemeyer, M.; Pieper, U.; Schmidt, H.-G.; Stalke, D.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1990**, 102, 941.
- (11) (a) Heckmann, G.; Niemeyer, M. J. *Am. Chem. Soc.* **2000**, 122, 4227. (b) Hasinoff, L.; Takats, J.; Zhang, X. W. *J. Am. Chem. Soc.* **1994**, 116, 8833.
- (12) (a) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, 326, 299. (b) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, 19, 2999.
- (13) Yao, S.; Chan, H.-S.; Lam, C.-K.; Lee, H. K. *Inorg. Chem.* **2009**, 48, 9936.
- (14) Shannon, R. D. *Acta Crystallogr.* **1976**, 32, 751.
- (15) (a) Hill, M. S.; Hitchcock, P. B.; Mansell, S. M. *Dalton Trans.* **2006**, 1544. (b) Whitener, G. D.; Hagadorn, J. R.; Arnold, J. J. *Chem. Soc., Dalton Trans.* **1999**, 1249. (c) Bai, S. D.; Guo, J. P.; Liu, D. S. *Dalton Trans.* **2006**, 2244.
- (16) Giesbrecht, G. R.; Shafir, A.; Arnold, J. J. *Chem. Soc., Dalton Trans.* **1999**, 3601.
- (17) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, 5, 1285.
- (18) (a) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Cerón, D. P.; Wang, J. *Dalton Trans.* **2010**, 6732. (b) Du, Z.; Zhang, Y.; Yao, Y.; Shen, Q. *Dalton Trans.* **2011**, 7639. (c) Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Wang, J. *Inorg. Chem.* **2007**, 46, 10022. (d) Deng, M. Y.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Chem. Commun.* **2004**, 2742.
- (19) Du, Z.; Zhou, H.; Yao, H.; Zhang, Y.; Yao, Y.; Shen, Q. *Chem. Commun.* **2011**, 3595.
- (20) (a) Tom Dieck, H.; Renk, I. W. *Chem. Ber.* **1971**, 104, 110. (b) Tom Dieck, H.; Franz, K.-D.; Hoffmann, F. *Chem. Ber.* **1975**, 108,

163. (c) Reinhold, J.; Benedix, R.; Birner, P.; Hennig, H. *Inorg. Chim. Acta* **1979**, *33*, 209.

(21) (a) Trifonov, A. A.; Borovkov, I. A.; Fedorova, E. A.; Fukin, G. K.; Larionova, J.; Druzhkov, N. O.; Cherkasov, V. K. *Chem.—Eur. J.* **2007**, *13*, 4981. (b) Trifonov, A. A. *Eur. J. Inorg. Chem.* **2007**, 3151. (c) Trifonov, A. A.; Shestakov, B. G.; Lyssenko, K. A.; Larionova, J.; Fukin, G. K.; Cherkasov, A. V. *Organometallics* **2011**, *30*, 4882. (d) Walter, M. D.; Berg, D. J.; Andersen, R. A. *Organometallics* **2007**, *26*, 2296. (e) Trifonov, A. A.; Gudilenkov, I. D.; Larionova, J.; Luna, C.; Fukin, G. K.; Cherkasov, A. V.; Poddelsky, A. I.; Druzhkov, N. O. *Organometallics* **2009**, *28*, 6707. (f) Trifonov, A. A.; Shestakov, B. G.; Gudilenkov, I. D.; Fukin, G. K.; Giambastiani, G.; Bianchini, C.; Rossin, A.; Luconi, L.; Filippi, J.; Sorace, L. *Dalton Trans.* **2011**, *40*, 10568.

(22) Cui, P.; Chen, Y.; Wang, G.; Li, G.; Xia, W. *Organometallics* **2008**, *27*, 4013.

(23) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192. (c) Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1585.