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Synthesis, reactivity and structural characterization of linked bis(amidinate) ytterbium complexes

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Abstract

Reaction of the dilithium salt of a linked bis(amidinate) dianionic ligand LLi_2 [L=Me₃SiNC(Ph)N(CH₂)₃NC(Ph)NSiMe₃] with anhydrous YbCl₃ in THF in 1:1 molar ratio, after crystallized from hexane, afforded the linked bis(amidinate) ytterbium chloride LYb(μ -Cl)₂YbL(THF) (1). The chloro bridges in complex 1 can be easily broken by donor solvent. Recrystallization of complex 1 from hexane in the presence of THF formed the monomeric ytterbium chloride LYbCl(THF)₂ (2). Reaction of complex 2 with 1 equiv. of CpNa, after workup, gave the desired ytterbium complex LYbCp(DME) (3) in high yield. All the complexes were characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction.

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1. Introduction

The application of amidinate ligands in organolanthanide or organolanthanoid chemistry has recently attracted much attention, since the electronic and steric effects of these ligands can be easily modified by the variation of the substituents on the N-atoms. A variety of lanthanide complexes supported by monoamidinate ligands have been synthesized [1–12], and some of them have been found to be effective initiators for the ring-opening polymerization of ε -caprolactone [1–3]. However, linked bis(amidinate) as ancillary ligands has relatively been seldom used in organolanthanide chemistry, there is only one paper concerning the synthesis and reactivity of this kind of lanthanide complexes [13]. Generally, linking two anionic ancillary ligands together by a bridge is a useful method of controlling complex geometry and limiting ligand mobility, which has been widely used in transitionmetal chemistry [14]. It is expected that the linked bis(amidinate) ligand system will form an interesting set of ancillary ligands for new lanthanide chemistry. Here, we describe the synthesis, reactivity and structure of three ytterbium complexes supported by a linked bis(amidinate) ligand.

2. Experimental

All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. LLi_2 [L=Me₃. SiNC(Ph)N(CH₂)₃NC(Ph)NSiMe₃] [15] and anhydrous YbCl₃ [16] were prepared according to the literature procedures. All other reagents were purchased from Acros and used as received without further purification. Melting points were determined in sealed Ar-filled capillary tubes. Ytterbium analysis was carried out by complexometric titration. Carbon, hydrogen and nitrogen analyses were preformed by direct combustion with a Carlo-Erba EA 1110 instrument. The IR spectra were recorded with a Magna-IR 550 spectrometer.

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2.1. Synthesis of complex $LYb(\mu-Cl)_2YbL(THF)$ (1)

Freshly prepared THF solution of LLi₂ (40 mL, 2.1 mmol) was added by syringe to a 100 mL Schlenk flask containing a suspension of YbCl₃ (0.59 g, 2.1 mmol) in THF. The reaction mixture was stirred for 48 h at room temperature, and then the solvent was removed in vacuum. The residue was extracted with hexane, and the precipitation was removed using a centrifuge. The extracts were concentrated and cooled to -15 °C. Complex 1 was obtained as yellow microcrystals in a few days (1.37 g, 49%). M.p.: 169-170 °C. Anal. Calc. (found) for C₅₀H₇₆₋ Cl₂N₈OSi₄Yb₂ (1334.53): C 45.00 (44.57), H 5.74 (5.45), N 8.39 (8.21), Yb 25.93 (25.62). IR (KBr pellet, cm^{-1}) 3062(m), 2954(s), 2873(m), 1674(m), 1613(s), 1493(m), 1445(m), 1358(m), 1252(m), 1062(m), 1046(m), 998(m), 898(w), 843(s), 783(w), 754(w), and 702(m). Recrystallization of complex 1 from hexane obtained the crystals suitable for an X-ray structure determination.

2.2. Synthesis of complex $LYbCl(THF)_2$ (2)

2.2.1. Method A

Microcrystals of complex **1** (1.33 g, 1.00 mmol) was dissolved in the hexane (15 mL), and than followed by addition of a small amount of THF (2 mL). The solution was concentrated and cooled to -15 °C for crystallization, the corresponding monomeric bis(amidinate) ytterbium chloride (**2**) was obtained as colorless crystals (0.88 g, 57%). M.p.: 126.5–127.4 °C. Anal. Calc. (found) for C₃₁H₅₀N₄O₂Si₂Yb (775.42): C 48.02 (47.65), H 6.50 (6.41), N 7.22 (7.18), Yb 22.32 (22.07). IR (KBr pellet, cm⁻¹): 3190(m), 2966(s), 2935(s), 2854(s), 1635(s), 1454(m), 1385(m), 1257(m), 1169(m), 1126(m), 1084(m), 1033(w), 995(w), 925(w), 856(w), 724(w), 686(w), and 547(w).

2.2.2. Method B

Freshly prepared solution of LLi₂ (81 mL, 2.1 mmol) in THF was added to a 100 mL Schlenk flask containing a solution of YbCl₃ (1.25 g, 4.5 mmol) in THF by syringe. The reaction mixture was stirred for 48 h at room temperature, and the solvent was removed in vacuum. The residue was extracted with hexane. The extracts were concentrated followed by addition of a small amount of THF and then cooled to -15 °C, complex **2** was obtained as colorless crystals (2.38 g, 53%).

2.3. Synthesis of complex LYbCp(DME) (3)

A THF solution containing CpNa (0.85 M, 1.0 mmol) was dropped into the THF solution of complex 2 (0.13 M, 1.0 mmol). The reaction mixture was stirred for 48 h at room temperature, and then the precipitation was separated from the reaction mixture by centrifugation. The solvent was removed in vacuum, and the residue was extracted with toluene (25 mL). The extracts were concentrated followed

by addition of a small amount of DME and cooled to -15 °C. Complex **3** was isolated as yellow crystals in a few days (0.99 g, 51%). M.p.: 131–132 °C. Anal. Calc. (found) for C₃₂H₄₉N₄O₂Si₂Yb (750.97): C 51.18 (50.88), H 6.58 (6.39), N 7.46 (7.52), Yb 23.04 (22.85). IR (KBr pellet, cm⁻¹): 2958(m), 1668(w), 1626(m), 1540(w), 1384(w), 1251(m), 1058(w), 890(w), 8431(m), and 700(m).

2.4. X-ray crystallography

Crystals suitable for X-ray diffraction of complexes 1–3 were sealed in a thin-walled glass capillary filled under argon for structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using sHELXS-97 programs. Crystal and refinement data are listed in Table 1. CCDC 261698-261700 for complexes 1-3 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www. ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internet.): +44 1223/336 033; e-mail: deposit@ccdc. cam.ac.uk].

3. Results and discussion

3.1. Synthesis and reactivity

A THF solution of LLi2 was added to a suspension of YbCl₃ in THF, the reaction mixture was stirred for 48 h, a clear solution was obtained. After workup, the linked bis(amidinate) lanthanide complex 1 was isolated from hexane as yellow microcrystals in moderately yield as shown in Scheme 1. Complex 1 was characterized by elemental analyses and IR spectrum. In the IR spectrum, there is strong absorption of C=N stretch at approximate 1640 cm^{-1} , which is consistent with the delocalized double bond of N–C–N linkage [17]. Further X-ray structure determination reveals that complex 1 has a dichloro bridged dinuclear structure. The chloro bridges in complex 1 can be easily broken by donor solvent. Recrystallization of complex 1 from hexane in the presence of a small amount of THF, the monomeric complex $LYbCl(THF)_2$ (2) was obtained. Furthermore, complex 2 can be also prepared by the direct metathesis reaction of YbCl₃ with LLi₂ in 1:1 molar ratio, and then crystallized from hexane in the presence of THF (Scheme 1). Elemental analyses are consistent with the structure with one linked bis(amidinate) ligand, one chlorine atom and two coordinated THF molecules at the metal center. There are characteristic absorptions of delocalized double bond of N-C-N in the IR

Table 1 Experimental data for the X-ray diffraction study of complex 1–3

	1	2	3	
Empirical formula	$C_{50}H_{76}Cl_2N_8OSi_4Yb_2$	$C_{31}H_{50}ClN_4O_2Si_2Yb$	$C_{32}H_{49}N_4O_2Si_2Yb$	
fw	1334.53	775.42	750.97	
Temperature (K)	193(2)	193(2)	193(2)	
Wavelength (Å)	0.71070	0.71070	0.71070	
Crystal system	Triclinic	Monoclinic	Monoclinic	
Space group	ΡĪ	C2/c	$P2_{1}/c$	
Unit cell dimensions				
a (Å)	10.9080(10)	37.622(4)	15.0391(19)	
<i>b</i> (Å)	13.1193(11)	10.1856(8)	14.3534(14)	
<i>c</i> (Å)	21.3691(18)	20.4986(19)	17.645(2)	
α (°)	94.594(2)	90	90	
β(°)	99.488(2)	113.852(2)	112.700(2)	
γ (°)	99.132(2)	90	90	
$V(Å^3)$	2960.2(4)	7184.3(12)	3513.8(7)	
Ζ	2	8	4	
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.497	1.434	1.420	
Abs coeff (mm^{-1})	3.352	2.776	2.762	
F(000)	1340	3160	1532	
θ Range	3.00-27.48	3.15-25.35	3.04-25.35	
Reflections collected	31,183	34,593	34,126	
Data/restraints/parameters	13236/0/641	6570/2/377	6405/4/366	
Goodness-of-fit on F^2	1.076	1.173	1.071	
$R[I > 2\sigma(I)]$	0.0368	0.0331	0.0433	
wR	0.0843	0.0656	0.1054	

spectrum. Complex **2** can be used as a useful precursor for the synthesis of linked bis(amidinate) lanthanide derivatives. Complex **2** smoothly reacted with 1 equiv. of CpNa in THF, after careful workup, to give the expected product LYbCp(DME), which was identified by elemental analyses and IR spectroscopy (Scheme 1).

Complexes 1–3 are extremely air- and moisture-sensitive, the crystals decompose in a few minutes when they are exposed to air, but crystals and solution showed no sign of decomposition after several months when stored in argon. These complexes are freely soluble in donor solvents such as THF and DME, and moderately soluble in toluene and benzene, and slightly in hexane. These complexes did not provide any resolvable ¹H NMR spectra, due to the strong paramagnetism of the ytterbium ion.

3.2. Crystal structure analyses

Although there are many structurally characterized amidinate lanthanide complexes in the literatures, there are only one example of structurally characterized lanthanide complexes supported by linked bis(amidinate) ligand. Hessen et al. previously reported the synthesis and structural characterization of a linked bis(amidinate) yttrium alkyl complex [13]. To elucidate the influence of the bridging linked bis(amidinate) on the lanthanide coordination sphere,



Scheme 1.



Fig. 1. Molecular structure of complex 1 showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

the X-ray crystal structures of complexes 1-3 were determined.

Crystals of complex 1 suitable for an X-ray structure determination were obtained from concentrated hexane solution at -15 °C. The molecular structural diagram of complex 1 is shown in Fig. 1, and the selected bond distances and bond angles are listed in Table 2. To our best knowledge, complex **1** is the first example of structurally characterized neutral amidinate lanthanide chloride, Edelmann et al. previously reported the crystal structures of 'ate' amidinate neodymium complexes [11]. Complex 1 is dinuclear linked by two chloro bridges in the solid state. The coordination environment around the two ytterbium atoms in complex 1 is inequivalent. The Yb(1) center is seven-coordinate with four nitrogen atoms, and two bridged chlorine atoms and one oxygen atom of THF molecule; while the Yb(2) atom is six-coordinate with four nitrogen atoms of the linked bis(amidinate) ligand, and two bridged chlorine atoms. Thus, the coordination geometries around two ytterbium centers for complex 1 are different. The coordination geometries about the ytterbium atoms can be best described as a distorted trigonal bipyramid for Yb(1)and a distorted tetrahedron for Yb(2), respectively, with each chelating bidentate amidinate ligand to occupy one coordination vertex. Two ytterbium atoms and two chlorine atoms are nearly coplanar with sum of the angles of 359.9° (Cl(1)-Yb(1)-Cl(2)=78.67(3), $Cl(2)-Yb(2)-Cl(1) = 80.58(3), Yb(2)-Cl(1)-Yb(1) = 100.62(3), and Yb(2)-Cl(2)-Yb(1) = 100.03(3)^{\circ}).$

The average bond distances of ytterbium atom to carbon atom on N–C–N linkage in each amidinate moiety are 2.701(4) and 2.705(9) Å, respectively, which indicate an η^3 -allyl structure [18]. These Yb–C bond distances are

Table 2			
Selected bond distances (Å)	and angles	(deg) for	complex 1

Yb(1)–N(1)	2.388(3)	Yb(1)–N(2)	2.277(3)
Yb(1)-N(3)	2.383(3)	Yb(1)–N(4)	2.309(3)
Yb(1)–C(1)	2.696(4)	Yb(1)–C(2)	2.704(4)
Yb(1)–O(1)	2.318(3)	Yb(1)–Cl(1)	2.6882(10)
Yb(1)-Cl(2)	2.7367(10)	Yb(2)–N(5)	2.330(3)
Yb(2)-N(6)	2.270(3)	Yb(2)–N(7)	2.333(3)
Yb(2)-N(8)	2.259(3)	Yb(2)-C(24)	2.704(4)
Yb(2)-C(25)	2.707(4)	Yb(2)–Cl(2)	2.6460(9)
Yb(2)–Cl(1)	2.6719(10)	N(2)-C(1)	1.321(5)
N(1)-C(1)	1.340(5)	N(4)–C(2)	1.321(5)
N(3)-C(2)	1.344(5)	N(6)-C(24)	1.304(5)
N(5)-C(24)	1.359(5)	N(8)-C(25)	1.306(5)
N(7)-C(25)	1.353(5)		
N(2)-Yb(1)-N(4)	75.90(12)	N(8)-Yb(2)-N(6)	75.78(13)
N(2)-Yb(1)-N(1)	57.58(12)	N(4)-Yb(1)-N(3)	57.24(12)
N(6)-Yb(2)-N(5)	58.37(12)	N(8)-Yb(2)-N(7)	58.38(12)
C(24)-Yb(2)-C(25)	98.36(12)	C(1)-Yb(1)-C(2)	131.45(12)
Cl(1)-Yb(1)-Cl(2)	78.67(3)	Cl(2)-Yb(2)-Cl(1)	80.58(3)
Yb(2)–Cl(1)–Yb(1)	100.62(3)	Yb(2)–Cl(2)–Yb(1)	100.03(3)
N(2)-C(1)-N(1)	115.4(4)	N(4)-C(2)-N(3)	115.1(4)
N(6)-C(24)-N(5)	114.8(4)	N(8)-C(25)-N(7)	114.9(3)



Fig. 2. Molecular structure of complex 2 showing atom-numbering scheme. Thermal ellipsoids are drawn at the 15% level. Hydrogen atoms are omitted for clarity.

slightly shorter than those observed in linked amidinate yttrium complex LY[CH(SiMe₃)₂](THF) (2.786(7) Å) [13], and homleptic unlinked amidinate ytterbium complexes $[CyNC(R)NCy]_3Yb$ (R=Me, Ph) (2.743(7) and 2.758(10) Å, respectively) [2]. The amidinate groups in complex 1 are unsymmetrically coordinated to the ytterbium atoms with the derivations rang from 0.04 to 0.11 Å. This coordination mode is similar to that observed in linked amidinate complex LY[CH(SiMe₃)₂](THF) [13], but different from those in unlinked amidinate lanthanide complexes [1,2]. Yb-N bond distances for the amidinate nitrogen atoms attached to the linker are shorter than those attached to the SiMe₃ groups, which can be attributed to the tethering of the amidinate groups. Associated with the tethering, the Yb-N-C-N torsion angles of 22.9 and 25.7°, respectively, are apparently larger than those in homoleptic amidinate lanthanide complexes [2]. The average Yb-N bond distances of 2.321(4) and 2.298(3) Å, respectively, are slighter shorter than the corresponding bond distance in the amidinate lanthanide complexes mentioned above. The Yb(1)-Cl(1) and Yb(1)-Cl(2) bond distances of 2.6882(10) and 2.7367(10) Å, respectively, indicate that two chlorine atoms are unsymmetrically coordinated to the ytterbium atom. The C-N bond distances within the chelating NCN unit are nearly equal and the average value is about 1.33 Å for both amidinate groups, which reflect the delocalization of the π bond in the N–C–N unit [19].

Crystals of complex **2** suitable for an X-ray structure determination were obtained from concentrated hexane-THF solution at -15 °C. The molecular structural diagram of complex **2** is shown in Fig. 2, with the selected bond distances and bond angles listed in Table 3. Complex **2** has a monomeric structure. The ytterbium atom is ligated by two linked bidentate amidinate moieties through nitrogen atoms, one chlorine atom, and two oxygen atoms of coordinated THF molecules. The chlorine atom is located cis to THF molecules, and two THF molecules are located trans positions. The coordination geometry about the ytterbium atom can be best described as a distorted trigonal bipyramid with each chelating bidentate amidinate ligand to occupy one coordination vertex, in which two amidinate groups and chlorine atom can be viewed as occupying equatorial positions, while two THF molecules occupy axial positions and the O(1)-Yb-O(2) angle is slightly distorted away from the idealized 180 to 177.96(10)°. This coordination geometry is similar to that of Yb(1) in complex 1, but different from that in LY[CH(SiMe₃)₂](THF) [13]. Teuben et al. previously reported the synthesis of amidinate yttrium chloride [PhC(NSiMe₃)₂]₂YCl(THF), in which there is only one coordinated THF molecule around the yttrium atom [4]; while there are two coordinated THF molecules in complex 2. This result revealed that using linked bis(amidinate) as ancillary ligand opens up the coordination sphere of

Table 3	
Selected bond distances (Å) and angles (deg) for complex 2	

Yb(1)–N(1)	2.404(3)	Yb(1)–N(2)	2.321(3)
Yb(1)–N(3)	2.434(3)	Yb(1)–N(4)	2.304(3)
Yb(1)–O(1)	2.327(3)	Yb(1)–O(2)	2.327(3)
Yb(1)-Cl(1)	2.6083(10)	Yb(1)–C(1)	2.788(4)
Yb(1)–C(2)	2.775(4)		
N(2)-Yb(1)-N(1)	56.48(11)	N(4)-Yb(1)-N(3)	56.12(11)
N(4)-Yb(1)-N(2)	73.63(12)	N(4)-Yb(1)-O(2)	89.96(12)
N(2)-Yb(1)-O(2)	89.25(12)	N(4)-Yb(1)-O(1)	89.85(11)
N(2)-Yb(1)-O(1)	92.64(12)	N(4)-Yb(1)-N(1)	130.08(11)
O(2)-Yb(1)-N(1)	91.02(11)	O(1)-Yb(1)-N(1)	90.66(11)
N(2)-Yb(1)-N(3)	129.70(11)	O(2)-Yb(1)-N(3)	88.89(11)
O(1)-Yb(1)-N(3)	89.32(10)	N(1)-Yb(1)-N(3)	173.80(10)



Fig. 3. Molecular structure of complex 3 showing atom-numbering scheme. Thermal ellipsoids are drawn at the 15% level. Hydrogen atoms are omitted for clarity.

ytterbium atom and allows for the coordination of an additional THF molecule.

The Yb(1)-C(1) and Yb(1)-C(2) bond distances of 2.788(4) and 2.775(4) Å, respectively, are apparently longer than the corresponding values observed in complex 1, but are comparable well with those bond distances in LY[CH(SiMe₃)₂](THF) [13] and [CyNC(R)NCy]₃Yb (R=Me, Ph) [2]. The average Yb-N bond length of 2.365(4) Å is also slightly longer than that observed in complex 1. The Yb(1)-Cl(1) bond distance of 2.6083(10) Å is shorter than the bridged Yb-Cl bond distances in complex 1. But this Yb(1)-Cl(1) distance is apparently longer than those terminal Yb-Cl bond distance found in {[(DIPPh)₂nacnac]YbCl(μ -Cl)₃Yb[(DIPPh)₂nacnac](THF)} and $(CH_3C_5H_4)[(DIPPh)_2nacnac]YbCl$ $[(DIPPh)_2 nacnac = N, N-diisopropylphenyl-2, 4-pentanedii$ mine anion] [20]. There is expected electron delocalization within the skeleton of the chelating NCN unit. The N(1)-Yb(1)-N(2) and N(3)-Yb(1)-N(4) bond angles are 56.48(11), and $56.12(11)^{\circ}$, respectively, which is in accordance with those angles in complex 1.

Crystals of complex **3** suitable for an X-ray structure determination were obtained from concentrated toluene-DME solution at -15 °C. The molecular structural diagram of complex **3** is shown in Fig. 3, with the selected bond distances and bond angles listed in Table 4. Complex **3** is a monomeric species. The ytterbium atom in complex **3** is nine-coordinate with the tetradentate linked bis(amidinate) group, one cyclopentadienyl group, and one coordinated DME molecule, the linker between two amidinate groups and the coordinated DME molecule are disordered due to strong thermal motion. The coordination geometry can be best described as a distorted trigonal bipyramid if the chelating bidentate amidinate ligands and the cyclopentadienyl group are considered to occupy one coordination vertex, in which two amidinate groups and one oxygen atom O(1A) can be viewed as occupying equatorial positions, while cyclopentadienyl group and other oxygen atom O(2A) occupy axial positions.

The Yb–C(Cp) bond lengths range from 2.618(8) to 2.654(8) Å, giving an average of 2.635(9) Å, which is comparable well with that in $(C_5H_5)YbCl_2(THF)_3$ [21,22]. The Yb(1)–C(1) and Yb(1)–C(2) bond distances are 2.816(5) and 2.839(7) Å, respectively, which are apparently longer than the corresponding values observed in complex 1, and slightly longer than those bond distances in complex 2, LY[CH(SiMe_3)_2](THF) [13] and [CyNC(R)NCy]_3Yb (R=Me, Ph) [2]. The Yb–N bond distances range from 2.252(8) to 2.542(5) Å, giving the average of 2.407(7) Å. This distance is apparently longer than those corresponding distances in complexes 1 and 2. Furthermore, the difference in Yb–N bond distance for the amidinate nitrogen atoms attached to the linker compared to those observed in

Table 4				
Selected bond	d distances (Å)	and angles	(deg) for	complex 3

Yb(1)–N(1)	2.542(5)	Yb(1)–N(2A)	2.301(8)
Yb(1)-N(4A)	2.252(8)	Yb(1)–N(3)	2.535(5)
Yb(1)-C(1)	2.816(5)	Yb(1)–C(2)	2.839(7)
Yb(1)-C(24)	2.654(9)	Yb(1)-C(25)	2.632(9)
Yb(1)-C(26)	2.618(8)	Yb(1)–C(27)	2.625(9)
Yb(1)-C(28)	2.648(8)	Yb(1)-O(1A)	2.482(7)
Yb(1)-O(2A)	2.524(8)		
N(4A)-Yb(1)-N(2A)	74.6(3)	N(3)-Yb(1)-N(1)	155.19(16)
N(4A)-Yb(1)-O(1A)	138.4(3)	N(4A)-Yb(1)-N(1)	128.0(2)
N(2A)-Yb(1)-O(1A)	139.4(3)	N(4A)-Yb(1)-O(2A)	95.3(3)
N(2A)-Yb(1)-O(2A)	94.7(3)	O(2A)-Yb(1)-N(1)	77.7(2)
N(2A)-Yb(1)-N(3)	130.6(2)	N(4A)-Yb(1)-N(3)	58.0(2)
N(2A)-Yb(1)-N(1)	55.1(2)	O(2A)-Yb(1)-N(3)	77.7(2)
O(1A)-Yb(1)-N(1)	85.30(19)	O(1A)-Yb(1)-N(3)	81.4(2)

complexes 1, 2, and LY[CH(SiMe₃)₂](THF) [13]. In complex 3, the derivations are 0.241 and 0.283 Å, respectively, while the values are 0.111 and 0.074 Å in complex 1, and 0.083 and 0.130 Å in complex 2, respectively. It is reasonable to ascribe the difference in bond parameters among these complexes to the increased steric congestion in complex 3 due to the replacement of chlorine atom by a cyclopentadienyl group. Associated with the increased steric congestion, the Yb–O(ether) bond distances apparently lengthened from about 2.30 Å in complexes 1 and 2 to about 2.50 Å in complex 3.

4. Conclusion

Three ytterbium complexes supported by a linked bis(amidinate) ligand were synthesized and structurally characterized. Reaction of freshly prepared LLi with anhydrous YbCl₃ in THF gave the corresponding linked bis(amidinate) ytterbium chloride. Crystallization from hexane afforded the ytterbium chloride as a dinuclear complex (1), while crystallization from hexane in the presence of THF gave the ytterbium chloride as a monomer (2). Complex 2 is a useful precursor for the synthesis of linked bis(amidinate) ytterbium derivatives. Reaction of complex 2 with 1 equiv. of CpNa afforded the expected product LYbCp(DME) (3). Furthermore, the crystal structure of the ytterbium chlorides represents the first examples of structurally characterized neutral amidinate lanthanide chloride.

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