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Ytterbium(II) Complex Bearing a Diaminobis(phenolate) Ligand: Synthesis, Structure, and One-Electron-Transfer and ϵ-Caprolactone Polymerization Reactions

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The first divalent ytterbium complex supported by a diaminobis(phenolate) ligand, $YbL(THF)_2 \cdot 0.5C_7H_8$ (**1**; THF = tetrahydrofuran), was synthesized in good yield by the amine elimination reaction of $Yb[N(SiMe_3)_2]_2(THF)_2$ with H_2L ($L = [Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}OC_6H_2\text{-}3,5\text{-}Bu^t_2)_2]$) in a 1:1 molar ratio. X-ray structural determination shows complex **1** to be a THF-solvated monomer, which adopts a distorted octahedral coordination geometry around the Yb atom. Complex **1** can react with PhNCO and PhC≡CH, as a single electron-transfer reagent, to give the corresponding reduction coupling product $[(YbLOCNPh)(THF)]_2 \cdot 4THF$ (**2**) and the alkynide complex YbLC≡CPh(DME) (**3**; DME = 1,2-dimethoxyethane). Complexes **2** and **3** have been characterized by X-ray crystal structural analysis. In complex **2**, the dianionic oxamide ligand resulting from the reductive coupling of two phenyl isocyanate molecules coordinates to two Yb atoms in a μ,η^4 fashion. Complex **3** has a monomeric structure with a Yb–C(terminal phenylacetynide) bond length of 2.374(3) Å. Complex **1** is also a highly efficient catalyst for ring-opening polymerization of ϵ-caprolactone.

Introduction

Over the last 20 years, the chemistry of lanthanide(II) complexes has made great progress. The use of substituted cyclopentadienyl (Cp)-based ligand systems, which show unique versatility in meeting the electronic and steric requirements necessary for stabilizing a wide variety of complexes, has been a significant factor contributing to the rapid development.[1] During the past decades, considerable attention has been turned to the development of lanthanide(II) complexes supported by ligand systems other than Cp anions. As a result, a variety of non-Cp ligands have been found to be suitable in stabilizing lanthanide(II) species, including amido,[2] phenoxide,[3] amidinato,[4] β-diketiminato,[5] bulky alkyl,[6] bridged diamido,[7] etc., and some of lanthanide(II) complexes displayed a rich chemistry[1,8] and a level of reactivity even higher than that of the Cp derivatives in the activation of dinitrogen.[9]

Bridged bis(phenolate) ligands have become increasingly popular in transition-metal and lanthanide(III) chemistry.[10]

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The tetradentate side-arm donor-bridged bis(phenolate) ligands, where the bracketed atoms are those capable of binding to the metal but the type of bond is not defined, therefore called a hemilabile functional group, have shown great potential applications in catalytic reactions promoted by groups 3 and 4 and lanthanide(III) metals. For example, the aminobis(phenolate)-based group 4 metal catalysts exhibit remarkably high activity and may be modified to give isospecific poly(1-hexene).[11] Alkoxyaminobis(phenolate) group 3 and lanthanide metal catalysts are highly active in the synthesis of heterotactic and sydiotactic poly(lactide) from *rac*- and *meso*-lactide, respectively,[10a,b] and syndiospecific poly(β-butyrolactone) from racemic β-butyrolactone.[10c] However, the application of these tetradentate bridged bis(phenolate) ligands in lanthanide(II) chemistry has been ignored to date. In continuing our research on the chemistry of bridged bis(phenolate)lanthanide(II) complexes,[3a] we have studied the synthesis of a ytterbium(II) complex with a diaminobis(phenolate) ligand and its reactivity. Here we report the synthesis and characterization of a monomeric ytterbium(II) complex YbL(THF)$_2$·0.5C$_7$H$_8$ (**1**; L = [Me$_2$NCH$_2$CH$_2$N(CH$_2$-2-OC$_6$H$_2$-3,5-Bu$^t{}_2$)$_2$]$^{2-}$; THF = tetrahydrofuran), which is very soluble in THF and soluble in hot toluene. The catalytic activity of complex **1** for the ring-opening polymerization of ϵ-caprolactone (ϵ-CL) is described, together with a study of its potential application as a one-electron-transfer reagent for the activation of organic molecules including reactions with phenyl isocyanate to a coupling product [(YbLOCNPh)(THF)]$_2$·4THF (**2**) and with phenylacetylene to an alkynide complex YbLC≡CPh(DME) (**3**; DME = 1,2-dimethoxyethane).

Experimental Section

General Procedures. All manipulations were performed under an Ar atmosphere, using standard Schlenk techniques. THF, DME, toluene, and hexane were distilled from sodium benzophenone ketyl before use. ϵ-CL was purchased from Acros, dried over CaH$_2$ for 48 h, and distilled under reduced pressure. PhNCO was purchased from Acros, dried over P$_2$O$_5$ for 48 h, and distilled under reduced pressure. PhC≡CH was purchased from Acros, dried over molecular sieves for 48 h, and distilled by vacuum. The starting complexes Yb[N(SiMe$_3$)$_2$]$_2$(THF)$_2$[12] and H$_2$L[13] were synthesized according to published methods. Lanthanide metal analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer.[14] Carbon and hydrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 Fourier transform IR spectrometer as KBr pellets. The melting points of complexes were measured in sealed capillaries and were uncorrected. ^{1}H NMR spectra were obtained on an INOVA 400 MHz apparatus and referenced to benzene-*d*. Molecular weights and molecular weight distributions were determined against polystyrene standards by gel permeation chromatography (GPC) at 30 °C on a Water 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4) using THF as the eluent. The molecular weights of polymers were corrected by a factor of 0.56.[15]

YbL(THF)$_2$·0.5C$_7$H$_8$ (1). A Schlenk flask was charged with H$_2$L (1.45 g, 2.77 mmol), toluene (15 mL), and a stirring bar. To this solution was added a toluene (20 mL) solution of Yb[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (1.76 g, 2.77 mmol), leading to the formation of a brown-red precipitate. The suspension was stirred at room temperature for 24 h. After centrifugation, the precipitate was dissolved in THF (30 mL) and concentrated. The orange-red microcrystals of **1** (1.50 g, 61% based on Yb) were obtained upon crystallization at −15 °C. Mp: 120−121 °C (dec). Elemental analysis and ^{1}H NMR for complex **1** with a half of toluene lost are as follows: Anal. Calcd for YbC$_{42}$H$_{70}$N$_2$O$_4$ (840.06): C, 60.05; H, 8.40; N, 3.33; Yb, 20.60. Found: C, 60.21; H, 8.11; N, 3.30; Yb, 20.97. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 6.80−7.15 (m, 4H, Ph), 3.60 (s, 4H, CH$_2$), 3.42 (m, 8H, CH$_2$), 2.50 (m, 4H, CH$_2$CH$_2$), 2.30 (s, 6H, CH$_3$), 1.73 (m, 8H, CH$_2$CH$_2$), 1.35 (s, 36H, C(CH$_3$)$_3$)). IR (KBr, cm^{-1}): 2956 (w), 2902 (w), 2871 (w), 1605 (m), 1474 (w), 1381 (m), 1304 (w), 1243 (m), 1196 (m), 1165 (m), 1111 (s), 1027 (m), 911 (s), 880 (m), 841 (m), 780 (s), 741 (m), 648 (s), 525 (m), 440 (m). Moreover, the free solvent complex YbL was obtained under vacuum for several hours. Elemental analysis and ^{1}H NMR for complex **1** with all solvent lost are as follows. Anal. Calcd for YbC$_{34}$H$_{54}$N$_2$O$_2$ (695.84): C, 58.69; H, 7.82; N, 4.03; Yb, 24.87. Found: C, 58.81; H, 7.63; N, 3.87; Yb, 25.04. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 6.80−7.15 (m, 4H, Ph), 3.60 (s, 4H, CH$_2$), 2.50 (m, 4H, CH$_2$CH$_2$), 2.30 (s, 6H, CH$_3$), 1.35 (s, 36H, C(CH$_3$)$_3$)). Crystals suitable for an X-ray diffraction analysis were obtained by crystallization at −15 °C from THF.

[(YbLOCNPh)(THF)]$_2$·4THF (2). To a solution of **1** (1.85 g, 2.09 mmol) in 20 mL of THF was slowly added PhNCO (0.23 mL, 2.09 mmol). The color of the solution changed from red to yellow immediately. The reaction was maintained for 24 h with

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Table 1. Experimental Data for the X-ray Diffraction of Complexes **1**−**3**

param	**1**	**2**	**3**
empirical formula	$C_{45.50}H_{74}N_2O_4Yb$	$C_{106}H_{166}N_6O_{12}Yb_2$	$C_{46}H_{69}N_2O_4Yb$
fw	886.11	2062.53	887.07
T (K)	193(2)	153(2)	153(2)
wavelength (Å)	0.710 70	0.710 70	0.710 70
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.6766(19)	11.7955(10)	20.1597(18)
b (Å)	14.893(3)	14.2426(13)	10.5615(8)
c (Å)	15.930(4)	16.2769(14)	23.409(2)
α (deg)	99.946(5)	80.499(4)	90
β (deg)	93.953(6)	76.699(4)	114.011
γ (deg)	94.277(4)	86.179(4)	90
V (Å^3)	2247.1(8)	2623.5(4)	4552.8(7)
Z	2	1	4
D_{calc} (Mg m^{-3})	1.310	1.305	1.294
abs coeff (mm^{-1})	2.122	1.831	2.095
F(000)	926	1080	1844
θ range (deg)	3.12−25.35	3.17−25.35	3.08−25.35
final R indices [$I > 2\sigma(I)$]	R1 = 0.0300 wR2 = 0.0739	R1 = 0.0253 wR2 = 0.0604	R1 = 0.0252 wR2 = 0.0576

stirring at room temperature. After removal of THF by vacuum, a yellow solid was obtained. The solid was dissolved in DME with a small amount of THF. Colorless crystals of **2** were obtained (1.36 g, 63% based on Yb) from THF (2 mL)−DME (8 mL) at room temperature. Mp: 164−166 °C (dec). Anal. Calcd for $Yb_2C_{90}H_{134}N_6O_8$-(1774.14): C, 60.93; H, 7.61; N, 4.74; Yb, 19.51. Found: C, 60.04; H, 7.55; N, 4.54; Yb, 19.32. IR (KBr, cm^{-1}): 3419 (s), 2963 (w), 1728 (w), 1620 (s), 1497 (s), 1389 (s), 1258 (w), 1157 (m), 1119 (w), 887 (w), 841 (w), 748 (w), 594 (m), 432 (w). Crystals suitable for X-ray analysis were grown in THF−DME at room temperature.

YbLC≡CPh(DME) (3). To a solution of **1** (1.94 g, 2.19 mmol) in 20 mL of THF was added PhC≡CH (0.24 mL, 2.19 mmol) slowly. The color of the solution changed from red to black immediately. The reaction was maintained for 24 h with stirring at room temperature. After removal of THF by vacuum, a brown solid was dissolved in hexane with a small amount of DME, and colorless crystals of **3** were obtained (1.15 g, 59% based on Yb) from DME (4 mL)−hexane (4 mL) upon crystallization at 0 °C. Mp: 181−182 °C (dec). Anal. Calcd for $YbC_{46}H_{69}N_2O_4$(887.07): C, 62.28; H, 7.84; N, 3.16; Yb, 19.51. Found: C, 62.40; H, 7.95; N, 3.03; Yb, 19.56. IR (KBr, cm^{-1}): 3453 (m), 2954 (m), 1479 (m), 1360 (w), 1235 (s), 1213 (s), 1155 (s), 1026 (w), 877 (w), 837 (w), 757 (w), 639 (m), 555 (m), 503 (s). Crystals suitable for X-ray analysis were grown from DME−hexane at 0 °C.

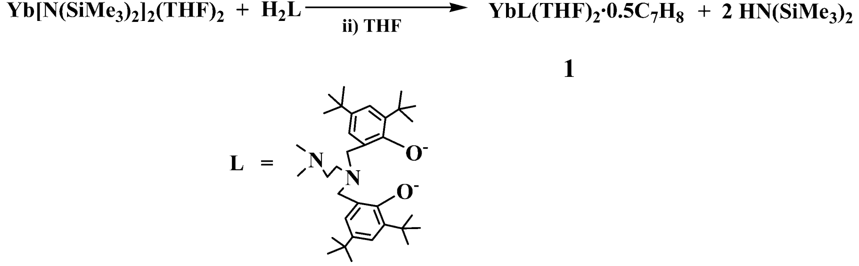
X-ray Crystallography. Suitable single crystals of complexes **1**−**3** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected on a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.710 70 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-H atoms were refined anisotropically. The H atoms 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 C atoms. All of 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 using the *SHELEXL-97* program.

Results and Discussion

Synthesis and Structure of 1. The amine elimination reaction was used for the synthesis of complex **1**. Thus, treatment of the ligand H_2L with $Yb[N(SiMe_3)_2]_2(THF)_2$ in a 1:1 molar ratio in toluene at room temperature, after workup, afforded complex **1** as orange-red crystals in good yield. Complex **1** was characterized by elemental analysis, ^{1}H NMR spectral analysis, and X-ray diffraction (Scheme 1). Complex **1** loses a half of toluene under gentle evacuation. So, satisfactory elemental analysis for complex **1** without a half of toluene can be obtained by careful treatment of the sample. Moreover, the crystals of complex **1** lose all of the solvated solvent easily under vacuum to become an unsolvated complex YbL as an orange-red powder. In the former case, the ^{1}H NMR spectrum shows signals at δ 3.42 and 1.73 for solvated THF, while no signals for THF were observed in the latter one. Complex **1** is well soluble in THF, soluble in hot toluene, but not soluble in cold toluene and hexane. The solubility of complex **1** is much better than that

Scheme 1



$$Yb[N(SiMe_3)_2]_2(THF)_2 + H_2L \xrightarrow[\text{ii) THF}]{\text{i) toluene}} YbL(THF)_2{\cdot}0.5C_7H_8 + 2\,HN(SiMe_3)_2$$

1

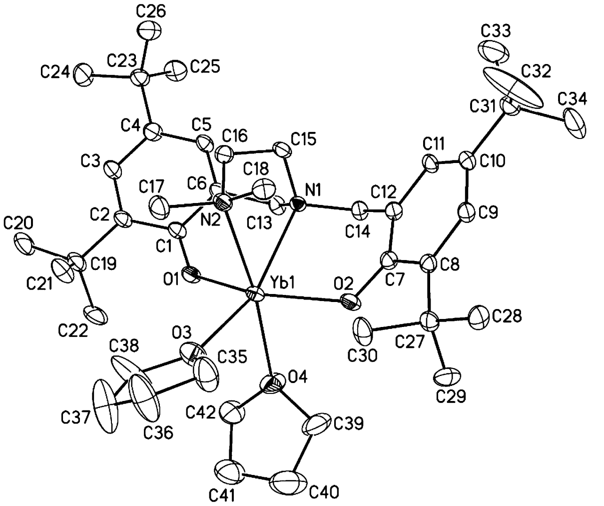


Figure 1. Molecular structure of complex **1** with a 30% probability level. H atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **1**

Yb1−O1	2.270(2)	Yb1−O3	2.502(3)
Yb1−O2	2.284(2)	Yb1−N1	2.554(3)
Yb1−O4	2.414(3)	Yb1−N2	2.603(3)
O1−Yb1−O2	151.16(9)	O4−Yb1−N1	119.75(10)
O1−Yb1−O4	88.94(9)	O3−Yb1−N1	155.37(10)
O2−Yb1−O4	84.35(9)	O1−Yb1−N2	92.46(9)
O1−Yb1−O3	101.06(10)	O2−Yb1−N2	98.97(9)
O2−Yb1−O3	106.20(10)	O4−Yb1−N2	169.99(10)
O4−Yb1−O3	84.87(11)	O3−Yb1−N2	85.14(10)
O1−Yb1−N1	80.20(8)	N1−Yb1−N2	70.23(9)
O2−Yb1−N1	78.96(8)		

of the C-bridged bis(phenolate)ytterbium(II) complexes reported.[3a]

Single-crystal X-ray diffraction showed that complex **1** possesses a THF-solvated monomeric structure with a half toluene in a unit cell (Figure 1). A six-coordinated Yb atom adopts a distorted octahedral geometry, in which O1, N1, O2, and O4 can be considered to occupy equatorial positions and O3 and O5 occupy axial positions. The C-bridged ytterbium(II) complexes were reported to have dimeric structures.[3a] The difference in the solid-state structure between complex **1** and C-bridged bis(phenolate)ytterbium(II) complexes should be attributed to the presence of the coordination of N atoms on the bridge to Yb atoms, which may provide steric protection against the formation of a dimer.

Selected bond distances (Å) and angles (deg) for complex **1** are listed in Table 2. The Yb−OAr bond lengths of 2.270(2) and 2.284(2) Å and the average of 2.277(2) Å are close to lengths of 2.201(2) and 2.349(2) Å and the average of 2.275(2) Å for C-bridged ytterbium(II) complex [Yb{CH_2-(2-OC_6H_2Me-4-Bu^t-6)$_2$}(THF)(HMPA)]$_2$.[3a] The values can also compare with those found in the other ytterbium(II) complexes with unbridged aryloxides [Yb(OAr)(μ-OAr)]$_2$ [2.10(2) Å],[3b] Yb(OAr)$_2$(THF)$_3$ [2.202(6) Å],[3c] Yb(Odpp)$_2$-(THF)$_3$ [2.207(3) Å],[3d] and [Yb(Odpp)(μ-Odpp)]$_2$ [2.11(2) Å], where Odpp = $OC_6H_3Ph_2$-2,6,[3e] when the effect of the coordination number on the effective ionic radii is considered.[16] The length of the Yb−N bond can only be compared with those for the trivalent complexes because there is no such kind of divalent complex reported. The bond lengths of Yb−N in complex **1** are 2.554(3) and 2.603(3) Å [average 2.579(3) Å], which are shorter than 2.484(3) and 2.518(3) Å [average 2.501(3) Å] found in a diaminobis(phenolate)-ytterbium(III) chloride complex,[10d] when the difference in the ionic radii between Yb(II) and Yb(III) is considered. (The ion radius of Yb(II) is 0.152 Å bigger than that of Yb(III) when Yb is six-coordinated.[16])

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Yb1−O2	2.101(2)	Yb1−N1	2.582(2)
Yb1−O1	2.104(2)	Yb1−N2	2.657(2)
Yb1−O3	2.233(2)	O3−C35	1.273(3)
Yb1−O4	2.452 (2)	N3−C35	1.305(3)
Yb1−N3A	2.497(2)	C35−C35A	1.507(5)
O3−C35−N3	127.9(2)	O3−Yb1−N3A	67.54(7)
O3−C35−C35A	117.1(3)	C35−N3−C36	113.1(2)
N3−C35−C35A	115.0(3)	C36−N3−Yb1A	131.64(16)
C35−O3−Yb1	124.77(16)	O2−Yb1−O1	153.40(7)
C35−N3−Yb1A	115.15(16)		

One-Electron-Transfer Reactions. 1. Reaction of 1 with PhNCO. The samarium(II) complexes Sm(MeC_5H_4)$_2$(THF)$_2$[17] and Sm(ArO)$_2$(THF)$_3$ (ArO = 2,6-di-*tert*-butyl-4-methylphenoxide)[18] were reported to react with PhNCO, as a single electron-transfer agent, yielding the corresponding reduction coupling products [Sm(MeC_5H_4)$_2$OCNPh]$_2$ (**4**)[19a] and [Sm-(ArO)$_2$OCNPh]$_2$ (**5**).[19b] To understand the electron-transfer properties of ytterbium(II) bis(phenolate), the reaction of complex **1** with PhNCO in a molar ratio of 1:1 was examined in THF at room temperature. The reaction went smoothly, and the color change from red to yellow was observed as the reaction proceeded. After workup, colorless crystals were obtained from THF−DME in high yield at room temperature. The crystals were characterized as complex **2** by elemental analysis and X-ray determination (Scheme 2). Obviously, complex **2** was formed via two one-electron reductions (2Yb(II) → 2Yb(III) + 2e) plus coupling from two phenyl isocyanate molecules by two complexes **1**. The reduction coupling reaction of PhNCO by the ytterbium(II) complex presented here is closely analogous to that by the samarium(II) complex.[17,18] The molecular structure of complex **2** is shown in Figure 2. Selected bond distances (Å) and angles (deg) are listed in Table 3. There are four free THF molecules in a unit cell. So, many free THF molecules existed in the molecule of complex **2**, making the determination of its crystal structure as well as elemental analysis very difficult. Satisfactory elemental analysis data can only be obtained by very careful treatment of the sample.

Complex **2** has a crystallographic C_{2h} symmetry, with the mirror plane containing C35, N3, O3, and Yb1 and phenyl rings. The C_2 axis bisects the C35−C35A bond. The C35−C35A bond length of 1.507(5) Å in complex **2** is that of a single bond. The C35−O3 and C35−N3 bond lengths, 1.273-

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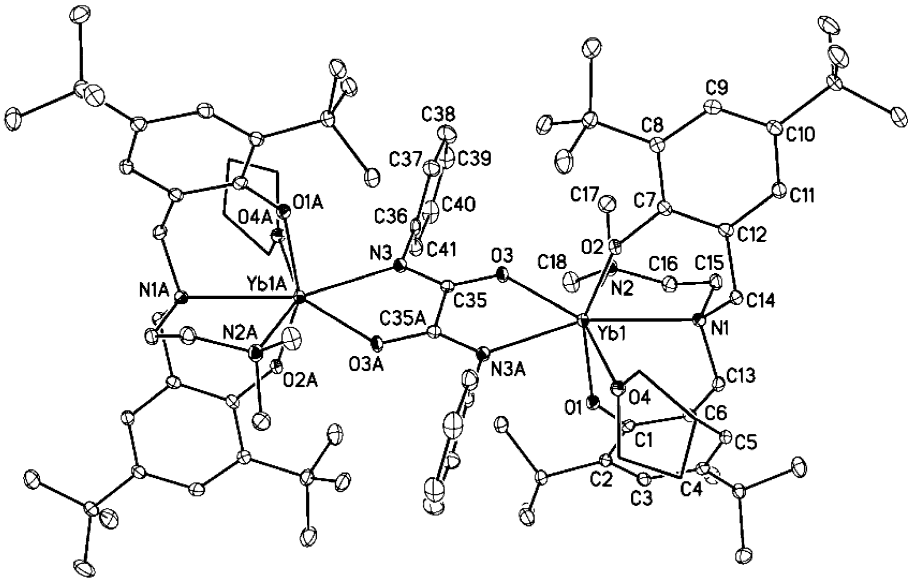

Figure 2. Molecular structure of complex **2** with a 30% probability level. H atoms are omitted for clarity.

Scheme 2

$$2\mathrm{YbL(THF)_2{\cdot}0.5C_7H_8} + 2\mathrm{PhNCO} \xrightarrow[\text{ii) DME-THF}]{\text{i) THF}} [\mathrm{(YbLOCNPh)(THF)}]_2{\cdot}4\mathrm{THF}$$

1 **2**

(3) and 1.305(3) Å, respectively, are consistent with multiple-bond character delocalized over the N−C−O unit. The bond lengths of Yb−O3 = 2.233(2) Å and Yb−N3 = 2.497(2) Å are longer than those for the typical trivalent Yb−OR [Yb−O1 = 2.104(2) Å and Yb−O2 = 2.101(2) Å in complex **2**] and Yb−NR$_2$ single-bond length [Yb−NPh$_2$ = 2.256(3) Å in the diaminobis(phenolate)ytterbium(III) amide complex[10d]] but shorter than the corresponding dative bond lengths [Yb−O4 = 2.452(2) Å, Yb−N1 = 2.582(2) Å, and Yb−N2 = 2.657(2) Å]. These bond parameters indicate that a [(PhN)OCCO(NPh)]$^{2-}$ dianion in complex **2** highly delocalizes its electrons (Figure 3). The structural character of complex **2** is quite similar to that for complexes **4** and **5** as well as [Sm(C$_5$Me$_5$)$_2$]$_2$[μ-η^4-(PhN)OCCO(NPh)]·2C$_7$H$_8$, which was formed by the reaction of Sm(C$_5$Me$_5$)$_2$(μ-η^1:η^1-PhN$_2$Ph) with CO.[19c]

2. Reaction of 1 with Phenylacetylene. The reaction of Yb(C$_5$Me$_5$)$_2$(OEt$_2$) with phenylacetylene was addressed to give the mixed-valent ytterbium phenylacetynide Yb$_3$(C$_5$Me$_5$)$_4$(μ-C≡CPh)$_4$ (**6**)[20] presumably by way of prior acetylene coordination, while the same reaction with the divalent samallocene afforded the trivalent phenylacetynide complex [SmCp′$_2$(μ-C≡CPh)]$_2$ for Cp′ = C$_5$H$_4{}^t$Bu[21] and SmCp′$_2$(C≡CPh)(THF) for Cp′ = C$_5$Me$_5$.[22] To see the electron-transfer property of the divalent ytterbium(II) complex supported by a bridged bis(phenolate) ligand, the reaction of complex **1** with phenylacetylene has been examined. Complex **1** does react with PhC≡CH in a 1:1 molar ratio in THF at room temperature. After concentration and treatment with a small amount of DME, colorless crystals were obtained in high yield. Single crystals suitable for X-ray diffraction studies were obtained from hexane−DME and have been identified as the monomeric ytterbium alkynide **3** (Scheme 3). The molecular structure of complex **3** is shown in Figure 4. The central Yb atom is coordinated by a bridged biphemolate group, a terminal phenylacetynide anion, and a DME molecule. The coordinated geometry around the Yb atom can be described as an approximate face-capped trigonal prism with the face-capping atom N1. The dimeric structure

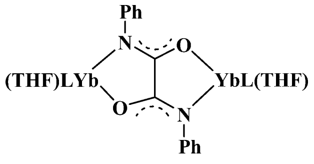

Figure 3. Bond fashion of a dianionic ligand in **2**.

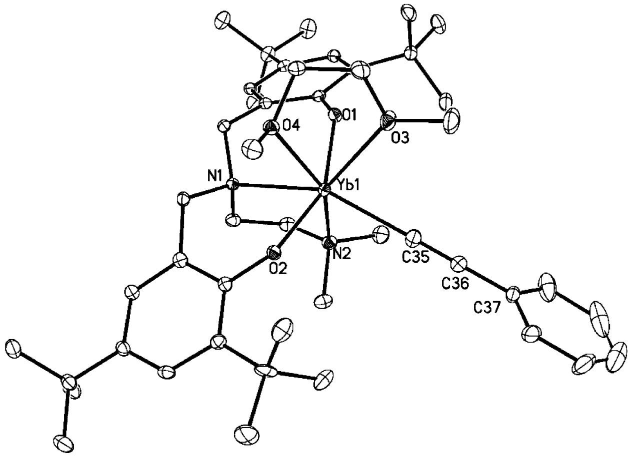

Figure 4. Molecular structure of complex **3** with a 30% probability level. H atoms are omitted for clarity.

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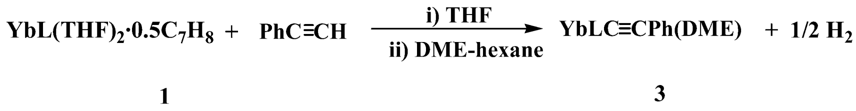
Scheme 3



$$\underset{\mathbf{1}}{YbL(THF)_2\cdot 0.5C_7H_8} + PhC\equiv CH \xrightarrow[\text{ii) DME-hexane}]{\text{i) THF}} \underset{\mathbf{3}}{YbLC\equiv CPh(DME)} + 1/2\ H_2$$

with bridged alkynides is popular for lanthanide alkynide complexes; in contrast, the monomeric structure is rare.[22,23] The monomeric structure here may be attributed to the bulky bis(phenolate) ligand and the coordination of DME, which makes the formation of alkyne bridges impossible. The ytterbium alkynide complexes are rare. To our best knowledge, this is the second complex structurally characterized to date; the first is a mixed-valent complex **6**.[20] So, the Yb(III)−C(C≡CPh) bond length can only be compared with those for other monomeric lanthanide alkynides. Selected bond distances (Å) and angles (deg) for complex **3** are listed in Table 4. The Yb−C35 bond length of 2.374(3) Å is comparable to 2.419(6) Å for $Sm(C_5H_5)_2(C\equiv CMe_3)$[23a] and 2.448(4) Å for $Y[Me_2Si(NCMe_3)(OCMe_3)]_2C\equiv CPh(THF)$,[23b] when differences in the ionic radii are considered. Although the value is shorter than 2.49(2) and 2.494(9) Å published for $Sm(C_5Me_5)_2(C\equiv CPh)(THF)$[22] and $Sm(Tp^{Me2})_2(C\equiv CPh)$,[23c] respectively, the two data for Sm−C(terminal alkynide) were regarded as unusually long. The bond length of Yb−C [2.374(3) Å] in complex **3** is shorter than that of Yb(III)−C(C≡CPh) [2.40(2) Å] in complex **6**; this is reasonable because the bond length of Yb−C(terminal alkynide) normally is shorter than that of Yb−C(bridged alkynide). The average bond length of Yb−OAr [2.105 (2) Å] is very close to those found in complexes **1** and **2**, when the difference in the ionic radii between Yb(II) and Yb(III) is considered.[16]

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

Yb1−O2	2.088(2)	Yb1−N1	2.566(2)
Yb1−O1	2.122(2)	Yb1−O3	2.619(2)
Yb1−C35	2.374(3)	C35−C36	1.211(4)
Yb1−O4	2.459(2)	C36−C37	1.437(4)
Yb1−N2	2.551(2)		
O2−Yb1−O1	153.20(7)	O4−Yb1−N1	82.94(6)
O2−Yb1−C35	95.56(9)	O2−Yb1−O3	115.80(7)
O1−Yb1−C35	111.17(9)	O1−Yb1−O3	74.85(7)
O2−Yb1−O4	79.24(7)	C35−Yb1−O3	74.77(9)
C35−Yb1−O4	128.04(9)	O4−Yb1−O3	62.37(6)
O2−Yb1−N2	94.13(7)	N2−Yb1−O3	141.68(7)
O1−Yb1−N2	89.20(7)	N1−Yb1−O3	137.46(6)
C35−Yb1−N2	79.23(9)	C36−C35−Yb1	176.2(3)
O4−Yb1−N2	152.18(7)	C35−C36−C37	179.2(3)
O2−Yb1−N1	77.58(7)	C35−Yb1−N1	146.94(9)
O1−Yb1−N1	78.81(7)		

Complexes **1**−**3** are very sensitive to air and moisture. Complexes **2** and **3** did not provide any resolvable ^1H NMR spectra because of the strong paramagnetism of the Yb(III) ions.

Catalytic Activity of Complex 1 for Ring-Opening Polymerization of ϵ-CL. To identify whether the ligand set L can stabilize the new ytterbium (II) based catalyst, the catalytic activity of complex **1** was tested for the ring-opening polymerization of ϵ-CL. The preliminary results are listed in Table 5. The data previously reported with some other ytterbium(II) complexes were also included for comparison. It can be seen that complex **1** shows extremely high activity. The polymerization was completed in 30 min at ambient temperature when the molar ratio of [CL] to [I] (I indicates complex **1**) is 3000:1, and even when the molar ratio of [CL] to [I] increases to 3500:1, the polymerization still gives a yield as high as 73.7% within 30 min under the same conditions. The activity is much higher than those found for complexes $Yb(ArO)_2(THF)_2$ (entry 4), $[Yb(MBMP)(THF)_2]_2$ (entry 5),[3a] and $Yb(C_5H_9C_9H_6)(THF)_2$ (entry 6)[24] and even comparable with that of $Sm(ArO)_2(THF)_3$ (entry 7).[25] However, the degree of control of the polymerizations performed with complex **1** is much lower than that afforded by $Sm(ArO)_2(THF)_3$. In fact, the molecular weights of the resulting polymers are always much lower than those expected from the monomer-to-initiator ratio and the molecular weight distributions are broader than those obtained with $Sm(ArO)_2(THF)_3$. These observations suggest that transfer reactions may take place with complex **1**.

Conclusion

The first ytterbium(II) complex supported by a diaminobis(phenolate) ligand, **1**, has been synthesized in high yield by the amine elimination reaction. Complex **1** can react with PhNCO and phenylacetylene as a one-electron-transfer reagent to give the corresponding complexes of **2** and **3**. Complex **1** exhibits extremely high activity for the ring-opening polymerization of ϵ-CL. The results indicate that improved catalytic behavior is shown by the ytterbium(II) complex supported by a tetradentate bis(phenolate) ligand bearing side-arm donors.

Table 5. Polymerization of ϵ-CL Initiated by Divalent Lanthanide Complexes[a]

entry	initiator	T (°C)	[M]/[I]	t (h)	yield (%)	M_n ($\times10^{-4}$)[b]	PDI[b]	ref
1	**1**	20	1000	5 min	100	4.34	2.29	this work
2	**1**	25	3000	0.5	100	2.78	2.15	this work
3	**1**	25	3500	0.5	73.7	1.80	1.99	this work
4	$(ArO)_2Yb(THF)_2$	25	800	0.5	70			this work
5	$[(MBMP)Yb(THF)_2]_2$	40	300	2	45			3a
6	$(C_5H_9C_9H_6)_2Yb(THF)_2$	rt	300	1	91.6	1.31	1.71	24
7	$(ArO)_2Sm(THF)_2$	25	2000	5 min	100	62.6	1.56	25

[a] Polymerization conditions: [M] = 1 mol/L, with toluene as the solvent. [b] Measured by GPC at 30 °C in THF.

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Supporting Information Available: Crystallographic data for **1**−**3** and synthesis details. This material is available free of charge via the Internet at http://pubs.acs.org.

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