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Controlled Syntheses, Characterization, and Reactivity of Neutral and Anionic Lanthanide Amides Supported by Methylene-Linked Bis(phenolate) Ligands

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A series of neutral and anionic bis(phenolate) lanthanide amides were synthesized by general metathesis reactions, and their reactivity was explored. Protolytic ligand exchange reactions of MBMPH$_2$ (MBMP = 2,2′-methylene bis(6-tert-butyl-4-methyl-phenolate)) with [Ln{N(TMS)$_2$}$_2$(μ-Cl)(THF)]$_2$ (TMS = SiMe$_3$) afforded the desired bridged bis(phenolate) lanthanide chlorides [(MBMP)Ln(μ-Cl)(THF)$_2$]$_2$ [Ln = Nd (**1**), Yb (**2**)] in high isolated yields. These lanthanide chlorides were found to be useful precursors for the synthesis of the corresponding lanthanide derivatives. Reactions of **1** and **2** with 2 equiv of NaN(TMS)$_2$ in THF produced the expected neutral bis(phenolate) lanthanide amido complexes (MBMP)Ln[N(TMS)$_2$](THF)$_2$ [Ln = Nd (**3**), Yb (**4**)] in high yields. Whereas the reactions of **1** and **2** with LiN(TMS)$_2$ in a 1:4 molar ratio gave the anionic bis(phenolate) lanthanide amides as discrete ion-pair complexes [Li(THF)$_4$][(MBMP)Ln{N(TMS)$_2$}$_2$] [Ln = Nd (**5**), Yb (**6**)] in high isolated yields. Further study revealed that **5** and **6** can also be conveniently synthesized in high yields by the direct reactions of MBMPH$_2$ with [Ln{N(TMS)$_2$}$_2$(μ-Cl)(THF)]$_2$ in a 2:1 molar ratio, and then with 4 equiv of ^{n}BuLi. The reactivity of the neutral and anionic bis(phenolate) lanthanide amides was comparatively investigated. It was found that the insertion reactions of carbodiimide into the Ln–N bond of neutral lanthanide amido complexes **3** and **4** gave the anticipated bis(phenolate) lanthanide guanidinate complexes [(μ-O–MBMP)Nd{(^{i}PrN)$_2$CN(TMS)$_2$}]$_2$ (**7**) and (MBMP)Yb[(^{i}PrN)$_2$CN(TMS)$_2$] (**8**), respectively, in high yields, whereas the similar reaction of carbodiimide with anionic amido complex **5** provided the unexpected ligand-redistributed products, and the homoleptic ion-pair bis(phenolate) neodymium complex [Li(DME)$_2$(THF)][(MBMP)$_2$Nd(THF)$_2$] (**9**) was finally isolated as one of the products. Furthermore, the anionic bis(phenolate) lanthanide amides showed higher catalytic activity for the polymerization of ϵ-caprolactone than the neutral ones. All of the complexes were characterized with elemental analysis and IR spectra, and the definitive molecular structures of **1**–**3** and **5**–**9** were provided by single-crystal X-ray analyses.

Introduction

In recent years, bridged bis(phenolate) ligands have received considerable attention in organolanthanide chemistry because of their attractive features, such as being easily available, tunable, and even potentially recyclable, which allows for the systematic variation of the steric and electronic properties of the bisphenolic portion.[1−3] In particular, some of these bridged bis(phenolate) lanthanide complexes have shown great potential applications in catalytic reactions. For example, the amine bis(phenolate) group 3 and lanthanide metal complexes are highly active initiators for the synthesis of poly(ϵ-caprolactone) and poly(lactide), respectively,[1c,e,h,j] and syndiospecific poly(β-butyrolactone) from racemic β-butyrolactone,[1i] the sulfur-bridged bis(phenolate) lanthanide alkoxides formed in situ can also initiate the controlled polymerization of lactide.[3c] In addition, the divalent amine bis(phenolate) ytterbium complex can not only react with a lot of substances, as a single electron-transfer reagent to produce novel trivalent ytterbium species, but also can initiate ϵ-caprolactone polymerization with extremely high activity.[1l]

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Recently, we became interested in studying the synthesis and reactivity of organolanthanide complexes supported by bridged bis(phenolate) ligands and found that the lanthanide amides supported by diamino bis(phenolate) ligands are highly efficient initiators for ϵ-caprolactone polymerization, but the polymerization process is not well controlled.[1e] In contrast, the lanthanide alkoxides based on methylene-linked bis(phenolate) ligands show apparently lower activity for this polymerization, but the polymerization is in a controlled fashion.[2b,e] These differences prompted us to understand how the ancillary ligands and the active groups affect the reactivity of the organolanthanide complexes supported by bridged bis(phenolate) ligands. Therefore, we intend to synthesize the lanthanide amides containing methylene-linked bis(phenolate) ligands and/or the alkoxides containing amine bis(phenolate) ligands and to systematically investigate the structure/reactivity relationships to gain more insight into this problem. In addition, we recently reported the successful synthesis of neutral lanthanide complexes bearing diamino- or imidazolidine-bridged bis(phenolate) ligands by direct metathesis reactions.[1e,m] Thus, we also intend to expand this synthetic method to the methylene-linked bis(phenolate) ligand systems. Because the synthesis of neutral bridged bis(phenolate) lanthanide derivatives by general salt metathesis reactions seems to be problematic,[1f] most of these lanthanide complexes were synthesized by the reaction of the appropriate trivalent homoleptic lanthanide amide or alkyl with an equivalent LH_2 ligand via a protolytic ligand exchange reaction.[1b−d,i,j,3] In this article, some neutral and anionic lanthanide amides supported by methylene-linked bis(phenolate) ligands $MBMP^{2-}$ (MBMP = 2,2′-methylene bis(6-tert-butyl-4-methyl-phenolate)) were successfully synthesized by general metathesis reactions using the corresponding lanthanide chlorides as precursors, and the comparative studies on their reactivity for the activation reaction of carbodiimide and the polymerization of ϵ-caprolactone were explored. To our best knowledge, this is the first example that the neutral and anionic lanthanide derivatives stabilized by the same ancillary ligand can be synthesized in a controlled manner by general metathesis reactions by turning of the molar ratio of the reagents.[4] Here we report these results.

Experimental Section

Methylene-linked bis(phenol)s $MBMPH_2$, $HN(TMS)_2$ (TMS = $SiMe_3$), and diisopropyl carbodiimide are commercially available. All of the manipulations were performed under an argon atmosphere, using the standard Schlenk techniques. THF, toluene, DME, and hexane were distilled from sodium benzophenone ketyl before use. $[Ln\{N(TMS)_2\}_2(\mu\text{-}Cl)(THF)]_2$ (Ln = Nd, Yb),[5] $NaN(TMS)_2$,[6] and $LiN(TMS)_2$[7] were prepared according to the published procedures. $HN(TMS)_2$ was dried over CaH_2 for 4 days and distilled before use. ϵ-Caprolactone (ϵ-CL) (ACROS Co.) was dried over CaH_2 for 4 days at room temperature and then distilled under reduced pressure. Lanthanide analyses were performed by EDTA titration with an xylenol orange indicator and a hexamine buffer,[8] and chloride analyses were carried out using the Volhard method. The content of lithium was determined with a Hitachi 180−80 polarized Zeeman atomic absorption spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. Because of their paramagnetism, no resolvable NMR spectrum for these lanthanide complexes was obtained. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL/min at 40 °C.

Synthesis of $[(MBMP)Nd(\mu\text{-}Cl)(THF)_2]_2$ (1). To a THF solution of $[Nd\{N(TMS)_2\}_2(\mu\text{-}Cl)(THF)]_2$ (30 mL, 1.77 g, 1.55 mmol) was added a THF solution of $MBMPH_2$ (20 mL, 1.05 g, 3.10 mmol). The mixture was stirred overnight at room temperature, and then THF was evaporated completely in a vacuum. Toluene (20 mL) was added to extract the product, and blue crystals were isolated in 3 days (1.74 g, 85%). Mp: 183−185 °C. Anal. Calcd for $C_{62}H_{92}Cl_2Nd_2O_8$: C, 56.21; H, 7.00; Cl, 5.35; Nd, 21.78. Found: C, 55.96; H, 6.89; Cl, 5.12; Nd, 21.61. IR (KBr, cm^{-1}): 2955 (s), 2914 (s), 2872 (m), 1604 (m), 1465 (s), 1441 (s), 1387 (m), 1232 (s), 1202 (m), 860 (m), 768 (m), 619 (m).

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Synthesis of [(MBMP)Yb(μ-Cl)(THF)$_2$]$_2$ (2). The synthesis of **2** was carried out in the same way as that described for **1**, but [Yb{N(TMS)$_2$}$_2$(μ-Cl)(THF)]$_2$ (1.72 g, 1.43 mmol) was used instead of [Nd{N(TMS)$_2$}$_2$(μ-Cl)(THF)]$_2$. Orange-red microcrystals (1.56 g) were obtained from a concentrated toluene solution (79%). Mp: 175−177 °C. Anal. Calcd for $C_{62}H_{92}Cl_2O_8Yb_2$: C, 53.87; H, 6.71; Cl, 5.13; Yb, 25.04. Found: C, 53.63; H, 6.61; Cl, 4.98. Yb, 24.92. IR (KBr, cm^{-1}): 2955 (s), 2915 (s), 2871 (m), 1605 (m), 1469 (s), 1441 (s), 1389 (m), 1233 (s), 1202 (m), 862 (m), 769 (m), 619 (m). Crystals suitable for X-ray structure analysis were obtained in the concentrated toluene/THF solution.

Synthesis of (MBMP)Nd[N(TMS)$_2$](THF)$_2$ (3). To a THF solution of **1** (25 mL, 1.88 g, 1.39 mmol) was added a THF solution of NaN(TMS)$_2$ (2.1 mL, 2.78 mmol). The mixture was stirred overnight at room temperature, and a colorless gel-like precipitate formed gradually. THF was evaporated in a vacuum, and toluene (20 mL) was added to extract the product. Blue crystals were obtained from a concentrated toluene solution (about 12 mL) at −5 °C overnight (1.64 g, 75% based on neodymium). Mp: 168−170 °C. Anal. Calcd for $C_{37}H_{64}NNdO_4Si_2$: C, 56.44; H, 8.19; N, 1.78; Nd, 18.32. Found: C, 56.16; H, 7.94; N, 1.65; Nd, 18.19. IR (KBr, cm^{-1}): 2956 (s), 2919 (s), 2872 (s), 1629 (m), 1474 (m), 1443 (s), 1385 (s), 1234 (s), 1131 (m), 1084 (m), 868 (m), 758 (m).

Synthesis of (MBMP)Yb[N(TMS)$_2$](THF)$_2$ (4). The synthesis of **4** was carried out in the same way as that described for **3**, but **2** (1.95 g, 1.41 mmol) was used instead of **1**. Orange microcrystals (1.58 g) were obtained from a concentrated toluene solution (10 mL) (69% based on ytterbium). Mp: 154−156 °C. Anal. Calcd for $C_{37}H_{64}NO_4Si_2Yb$: C, 54.45; H, 7.90; N, 1.72; Yb, 21.20. Found: C, 54.27; H, 7.74; N, 1.64; Yb, 21.02. IR (KBr, cm^{-1}): 2956 (s), 2920 (s), 2871 (s), 1630 (m), 1474 (m), 1443 (s), 1387 (s), 1233 (s), 1130 (m), 1084 (m), 868 (m), 759 (m).

Synthesis of [Li(THF)$_4$][(MBMP)Nd{N(TMS)$_2$}$_2$] (5). Method A. To a solution of **1** (1.92 g, 1.45 mmol) in THF (25 mL) was added freshly prepared LiN(TMS)$_2$ in THF (30 mL, 5.80 mmol). The mixture was stirred overnight at room temperature, and the solvent was evaporated in a vacuum. Toluene (20 mL) was added to the residue, and the mixture was stirred at 80 °C for about 0.5 h. The precipitate formed was removed by centrifugation, and to the solution was added THF (0.5 mL). Blue crystals were obtained from the solution at −5 °C overnight (2.52 g, 79% based on neodymium). Mp: 128−130 °C. Anal. Calcd for $C_{51}H_{98}LiN_2NdO_6Si_4$: C, 55.74; H, 8.99; N, 2.55; Li, 0.63; Nd, 13.13. Found: C, 55.51; H, 8.75; N, 2.43; Li, 0.59; Nd, 12.89. IR (KBr, cm^{-1}): 2956 (s), 2915 (s), 2870 (s), 1639 (m), 1465 (s), 1440 (s), 1385 (m), 1253 (s), 1180 (m), 1050 (w), 929 (m), 845 (m).

Method B. To a THF solution of [Nd{N(TMS)$_2$}$_2$(μ-Cl)(THF)]$_2$ (30 mL, 2.23 g, 1.74 mmol) was added a THF solution of MBMPH$_2$ (20 mL 1.18 g, 3.48 mmol). The mixture was stirred for about 3 h at room temperature, and then the system was cooled to −10 °C. ^{n}BuLi in hexane (4.63 mL, 6.96 mmol) was added dropwise to the solution. The mixture was stirred at room temperature overnight, and then the solvent was evaporated in a vacuum. The following procedure is similar to that described for **Method A**, and **5** was isolated as blue crystals (2.21 g, 58%).

Synthesis of [Li(THF)$_4$][(MBMP)Yb{N(TMS)$_2$}$_2$] (6). The synthesis of **6** was carried out in the same way as that described for **5**, but **2** (2.15 g, 1.56 mmol) was used instead of **1**. After workup, pale yellow microcrystals were isolated from concentrated toluene/THF solution (2.67 g, 76% for **Method A**; 88% for **Method B**). Mp: 116−118 °C. Anal. Calcd for $C_{51}H_{98}LiN_2O_6Si_4Yb$: C, 54.32; H, 8.76; N, 2.48; Li, 0.62; Yb, 15.35. Found: C, 54.11; H, 8.58; N, 2.34; Li, 0.57; Yb, 15.23. IR (KBr, cm^{-1}): 2955 (s), 2915 (s), 2871 (s), 1637 (m), 1469 (s), 1441 (s), 1387 (m), 1253 (s), 1181 (m), 1050 (w), 933 (m), 843 (m).

Synthesis of [(μ-O−MBMP)Nd{(^{i}PrN)$_2$CN(TMS)$_2$}]$_2$ (7). To a THF solution of **3** (30 mL, 2.77 mmol) was added a THF solution of diisopropyl carbodiimide (5.5 mL, 2.77 mmol). The mixture was stirred overnight at room temperature, THF was evaporated in a vacuum, and then toluene (25 mL) was added to extract the product. The precipitate was removed by centrifugation, and blue crystals of **7** were obtained in 2 days at −5 °C in 72% yield by cooling the toluene solution (1.53 g). Mp: 182−184 °C. Anal. Calcd for $C_{72}H_{124}N_6Nd_2O_4Si_4$: C, 56.20; H, 8.12; N, 5.46; Nd, 18.75. Found: C, 55.96; H, 8.03; N, 5.35; Nd, 18.56. IR (KBr, cm^{-1}): 3209 (w), 2955 (s), 2916 (s), 2872 (s), 1651 (s), 1516 (s), 1465 (s), 1434 (s), 1390 (m), 1253 (m), 1171 (m), 1055 (w), 840 (m).

Synthesis of (MBMP)Yb[(^{i}PrN)$_2$CN(TMS)$_2$](THF)$_2$ (8). The synthesis of **8** was carried out as that described for **7**, but **4** (2.93 mmol) was used in place of **3**. After workup, orange microcrystals were obtained from concentrated toluene solution (1.60 g, 65%). Mp: 155−157 °C. Anal. Calcd for $C_{44}H_{78}N_3O_4Si_2Yb$: C, 56.08; H, 8.34; N, 4.46; Yb, 18.36. Found: C, 55.89; H, 8.22; N, 4.28; Yb, 18.17. IR (KBr, cm^{-1}): 3198 (w), 2954 (s), 2915 (s), 2873 (s), 1647 (s), 1515 (s), 1465 (s), 1434 (s), 1388 (m), 12543 (m), 1170 (m), 1055 (w), 840 (m). Crystals suitable for X-ray structure analysis were obtained by the slow cooling of a hot toluene solution.

Synthesis of [Li(DME)$_2$(THF)][(MBMP)$_2$Nd(THF)$_2$] (9). To a THF (30 mL) solution of **5** (2.67 g, 2.43 mmol) was added a THF solution of diisopropyl carbodiimide (4.9 mL, 2.43 mmol), and the mixture was stirred overnight at room temperature. The solution was concentrated to about 3 mL, and then DME (0.5 mL) and hexane (12 mL) were added. Pale-blue crystals were isolated in 2 days (1.15 g, 38%). Mp: 138−140 °C. Anal. Calcd for $C_{66}H_{104}LiNdO_{11}$: C, 64.73; H, 8.56; Li, 0.57; Nd, 11.78. Found: C, 64.49; H, 8.42; Li, 0.48; Nd, 11.57. IR (KBr, cm^{-1}): 2951 (s), 2912 (s), 1608 (w), 1466 (s), 1435 (s), 1385 (m), 1084 (s), 860 (m).

A Typical Polymerization Procedure. The procedures for the polymerization of ϵ-caprolactone initiated by **3**−**6** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of ϵ-caprolactone in toluene. To this solution was added the desired amount of initiator in toluene by syringe. The contents of the flask were then stirred vigorously at room temperature for the desired time. The reaction mixture was quenched by the addition of 1 M HCl-ethanol solution and then poured into methanol to precipitate the polymer, which was dried in a vacuum and weighed.

X-ray Crystallography. Suitable single crystals of **1**−**3** and **5**−**9** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.71070 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 Tables 1 and 2.

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 anisotropically. All of the hydrogen 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 *SHELEXL-97* programs.

Table 1. Crystallographic Data for **1**−**3** and **5**

compound	**1**	**2·3THF**	**3·**	**5**
formula	$C_{62}H_{92}Cl_2O_8Nd_2$	$C_{74}H_{116}Cl_2O_{11}Yb_2$	$C_{37}H_{64}NNdO_4Si_2$	$C_{51}H_{98}LiN_2O_6Si_4Nd$
fw	1324.74	1598.65	787.31	1098.85
T (K)	193(2)	193(2)	193(2)	193(2)
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$C2c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
crystal size (mm^3)	0.5 × 0.4 × 0.29	0.80 × 0.60 × 0.20	0.40 × 0.30 × 0.20	0.5 × 0.32 × 0.23
a (Å)	31.218(2)	12.223(4)	13.0248(11)	18.129(3)
b (Å)	12.2454(6)	12.914(4)	15.3911(12)	18.406(2)
c (Å)	22.4827(16)	14.009(4)	20.6746(18)	19.616(3)
α (deg)		75.536(11)		94.907(3)
β (deg)	132.0440(10)	66.365(10)	98.730(2)	102.577(4)
γ (deg)		77.705(13)		98.928(3)
V (Å^3)	6382.6(7)	1945.6(10)	4096.5(6)	6262.9(15)
Z	4	1	4	4
D_{calcd} (g cm^{-3})	1.379	1.364	1.277	1.165
μ(mm^{-1})	1.741	2.510	1.361	0.947
F(000)	2728	822	1652	2340
θ_{max} (deg)	27.48	27.48	25.35	25.35
collected reflns	34 535	21 232	39 132	62 193
unique reflns	7292	8518	7478	22 775
observed reflns [$I > 2.0\sigma(I)$]	6666	8328	6761	17 911
no. of variables	335	407	421	1212
GOF	1.074	1.058	1.143	1.096
R	0.0326	0.0298	0.0349	0.0495
wR	0.0787	0.0789	0.0724	0.0998

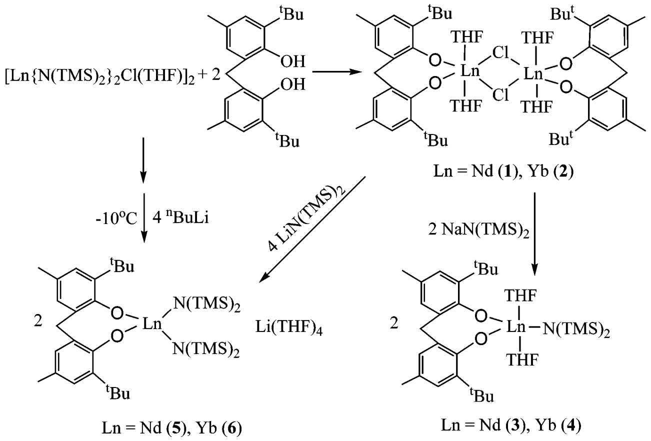
Table 2. Crystallographic Data for **6**−**9**

compound	**6**	**7·C_7H_8**	**8**	**9·THF**
formula	$C_{51}H_{98}LiN_2O_6Si_4Yb$	$C_{79}H_{132}N_6Nd_2O_4Si_4$	$C_{44}H_{78}N_3O_4Si_2Yb$	$C_{70}H_{112}LiNdO_{12}$
fw	1127.65	1630.75	942.31	1296.78
T (K)	193(2)	218(2)	218(2)	183(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
crystal size (mm^3)	0.40 × 0.30 × 0.20	0.30 × 0.30 × 0.20	0.40 × 0.30 × 0.15	0.70 × 0.25 × 0.20
a (Å)	18.0270(17)	13.9274(17)	11.6525(10)	18.3594(17)
b (Å)	18.3365(19)	12.1349(14)	27.241(2)	13.4459(11)
c (Å)	19.538(2)	25.304(3)	15.4738(14)	29.180(3)
α (deg)	94.434(2)			
β (deg)	102.595	97.616(3)	97.439(2)	100.059(3)
γ (deg)	98.967(3)			
V (Å^3)	6184.3(11)	4238.9(9)	4870.4(7)	7092.7(11)
Z	4	2	4	4
D_{calcd} (g cm^{-3})	1.211	1.278	1.285	1.214
μ(mm^{-1})	1.632	1.315	2.009	0.788
F(000)	2380	1712	1972	2764
θ_{max} (deg)	25.35	25.35	25.35	25.35
collected reflns	61 695	40 295	46 206	66 339
unique reflns	22 512	7753	8896	12 954
observed reflns [$I > 2.0\sigma(I)$]	17 670	6482	7877	10 788
no. of variables	1212	438	506	765
GOF	1.119	1.185	1.181	1.180
R	0.0492	0.0722	0.0499	0.0745
wR	0.0912	0.1340	0.1022	0.1442

Results and Discussion

Synthesis and Characterization of Neutral and Anionic Bis(phenolate) Lanthanide Amides. To synthesize the methylene-linked bis(phenolte) lanthanide amido complexes by salt metathesis reaction, the corresponding lanthanide chlorides with the general formula (MBMP)LnCl(THF)$_x$ should be prepared. However, these lanthanide chlorides cannot be synthesized by general salt metathesis reactions of anhydrous $LnCl_3$ with $MBMPNa_2$ in a 1:1 molar ratio.[2c] Thus, the protolytic ligand exchange reactions of [Ln{N(TMS)$_2$}$_2$(μ-Cl)(THF)]$_2$ with $MBMPH_2$ were used. With the addition of 2 equiv of $MBMPH_2$ to a THF solution of [Ln{N(TMS)$_2$}$_2$(μ-Cl)(THF)]$_2$, the color of the solution gradually changed to pale purple-blue (for neodymium) or brown (for ytterbium). After workup, the desired bis(phenolate) lanthanide chlorides with the general formula [(MBMP)Ln(μ-Cl)(THF)$_2$]$_2$ (Ln = Nd (**1**), Yb (**2**)) were obtained from a concentrated toluene solution in high isolated yields as analytically pure-blue or orange-red crystals as shown in Scheme 1. Elemental analyses revealed that the complex consists of one bis(phenolate) ligand, one chlorine atom, and two coordinated THF molecules at the metal center. Their definitive molecular structures were confirmed by single-crystal structure determination. **1** and **2** are

Scheme 1



relatively stable to air and moisture; the crystals can be exposed to air for 1 h without apparent deterioration. **1** and **2** are well soluble in THF and toluene.

1 and **2** are isostructural (Figure 1). Each complex shows a centrosymmetric dimeric structural feature containing a Ln_2Cl_2 core bridging through the chlorine atoms. The two bridging chlorine atoms and two lanthanide atoms are exactly coplanar, as required by the crystallographic symmetry. The central metal atom is six-coordinated with bis(phenolate) ligands, two chlorine atoms, and two THF molecules in a distorted octahedron, in which O(1), O(2), Cl(1), and Cl(1A) can be considered to occupy equatorial positions and O(3) and O(4) to occupy axial positions.

The average Nd−O(Ar) and Yb−O(Ar) bond lengths of 2.172(2) and 2.059(2) Å, respectively, are slightly smaller than the corresponding bond lengths observed in complexes $[(MBMP)Ln(\mu\text{-}O^iPr_2)(THF)_2]_2$ (2.215(5) Å for the neodymium complex and 2.120(3) Å for the ytterbium complex)[2b] and $[(EDBP)Nd(\mu\text{-}O^iPr)(THF)_2]_2$.(2.225(5) Å).[2e] Two chlorine atoms are unsymmetrically coordinated to the neodymium atoms with a deviation of 0.041 Å in **1** but symmetrically coordinated to the ytterbium atoms in **2**. The average Ln−Cl bond lengths of 2.8561(8) and 2.712(1) Å in **1** and **2**, respectively, are comparable with the bond lengths of the bridging Ln−Cl bonds reported in $[\{\mu_2\text{-}p\text{-}(Me_3SiN)_2C_6H_4\}Nd(\mu_2\text{-}Cl)(THF)]_4$ (2.828(2) Å),[9] $\{[(SiMe_3)_2NC(N^iPr)_2]_2Nd(\mu\text{-}Cl)\}_2$ (2.841(2) Å),[10] and $[(DIPPh)_2nacnac]YbCl(\mu\text{-}Cl)_3Yb[(DIPPh)_2nacnac](THF)$ (2.708(3) Å) ($(DIPPh)_2nacnac$ = *N*,*N*-diisopropylphenyl-2,4-pentanediimine anion).[11]

1 and **2** are good precursors for the synthesis of well-defined methylene-linked bis(phenolate) lanthanide amides by simple metathesis reactions. **1** and **2** reacted smoothly with 2 equiv of $NaN(TMS)_2$ in THF, after workup, to afford the corresponding neutral bis(phenolate) lanthanide amido complexes $(MBMP)Ln[N(TMS)_2](THF)_2$ (Ln = Nd (**3**), Yb (**4**)) in moderate isolated yields at room temperature. The compositions of **3** and **4** were confirmed with elemental analysis, and the definitive molecular structure of **3** was determined by single-crystal structure analysis.

The molecular structural diagram of **3** is shown in Figure 2 with its selected bond lengths and angles. **3** has a monomeric structure, which is different from the dimeric structure of the corresponding methylene-linked bis(phenolate) alkoxides[2b] and chlorides **1** and **2**. The neodymium atom is five-coordinated with two oxygen atoms from the bis(phenolate) ligands, one nitrogen atom from the amido group, and two oxygen atoms from two THF molecules to form a distorted trigonal bipyramid, in which O(1), O(2), and N(1) are considered to occupy the equatorial plane, and O(3) and O(4) occupy the apical positions.

In **3**, the averaged Nd−O(Ar) bond length of 2.200(2) Å is comparable with the corresponding values observed in **1**, and $(MBMP)Nd(C_5H_5)(THF)_2$ (2.173(3) Å),[2b] $[(EDBP)Nd(\mu\text{-}O^iPr)(THF)]_2$ (2.225(5) Å).[2e] The Nd−N(TMS) bond length of 2.352(3) Å is comparable with the corresponding bond length in $Nd[N(TMS)_2]_3$ (2.29(2) (Å))[12] when the effect of the coordination number on the effective ionic radius is considered.

Further study revealed that **1** and **2** can also react with 4 equiv of $LiN(TMS)_2$ under the same reaction conditions, to produce the anionic lanthanide amido complexes $[Li(THF)_4][(MBMP)Nd\{N(TMS)_2\}_2]$ [Ln = Nd (**5**), Yb(**6**)] in high isolated yields (Scheme 1). **5** and **6** were identified with elemental analysis, IR spectra, and single-crystal X-ray diffraction study. **5** and **6** are extremely sensitive to air and moisture. They are freely soluble in THF and moderately soluble in toluene and benzene but insoluble in hexane.

Furthermore, **5** and **6** can also be conveniently prepared by the direct reactions of $[Ln\{N(TMS)_2\}_2(\mu\text{-}Cl)(THF)]_2$ with $MBMPH_2$ in a 1:2 molar ratio and then with 4 equiv of ^{n}-BuLi in situ in THF and isolated from concentrated toluene solution in high yields, as shown in Scheme 1. These results demonstrated that the Ln−Cl bonds in the methylene-linked bis(phenolate) lanthanide chlorides have good reactivity for the chloride-substituted reaction, which are quite different from the cases of the yttrium and scandium diamino- bis(phenolate) chlorides, $[Y(O_2^{tBu}NN')(\mu\text{-}Cl)(py)]_2$ and $Sc(O_2^{tBu}NN')Cl(py)$ [$O_2^{tBu}NN'$ = $(2\text{-}C_5H_4N)CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2{}^tBu_2\text{-}3,5)_2\}$], in which the substitution of the chloride with a range of lithium or magnesium alkyls or $LiN(TMS)_2$ was unsuccessful.[1f]

5 crystallizes with two crystallographically independent but chemically similar molecules (**5a**, **5b**) in the unit cell. **5** and **6** are isostructural, and both have a discrete ion-pair structure. An ORTEP diagram of the anion is depicted in Figure 3, with the selected bond lengths and angles. In the anion, the central metal atom is four-coordinated with bis(phenolate) ligands and two trimethylsilylamido groups in a distorted tetrahedron. In the cation, the lithium atom is four-coordinated by four THF molecules to form a distorted tetrahedron.

In **5** and **6**, the average Nd−O(Ar) and Yb−O(Ar) bond lengths of 2.195(3), and 2.087(3) Å, respectively, are in

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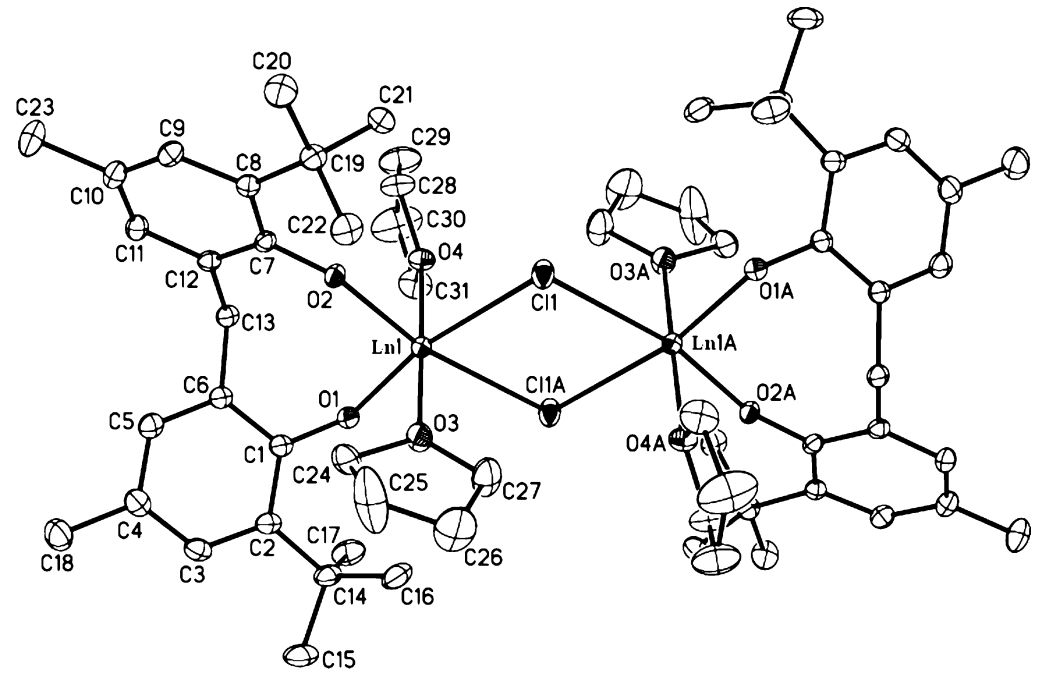

Figure 1. Molecular structure of [(MBMP)Ln(μ-Cl)(THF)$_2$]$_2$ (Ln = Nd (**1**), Yb (**2**)). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) (with data for **2** in parentheses): Ln(1)−O(1) 2.189(2) [2.058(2)], Ln(1)−O(2) 2.155(2) [2.061(2)], Ln(1)−Cl(1) 2.8767(8) [2.7139(10)], Ln(1)−Cl(1A) 2.8354(8) [2.7107(11)]; O(1)−Ln(1)−O(2) 97.68(8) [98.72(9)], O(1)−Ln(1)−Cl(1A) 93.79(6) [92.54(7)], O(2)−Ln(1)−Cl(1) 92.32(5) [90.90(7)], Cl(1A)−Ln(1)−Cl(1) 76.58(2) [77.85(3)], O(3)−Ln(1)−O(4) 178.15(8) [176.69(8)], Ln(1)−Cl(1)−Ln(1A) 103.42(2) [102.15(3)].

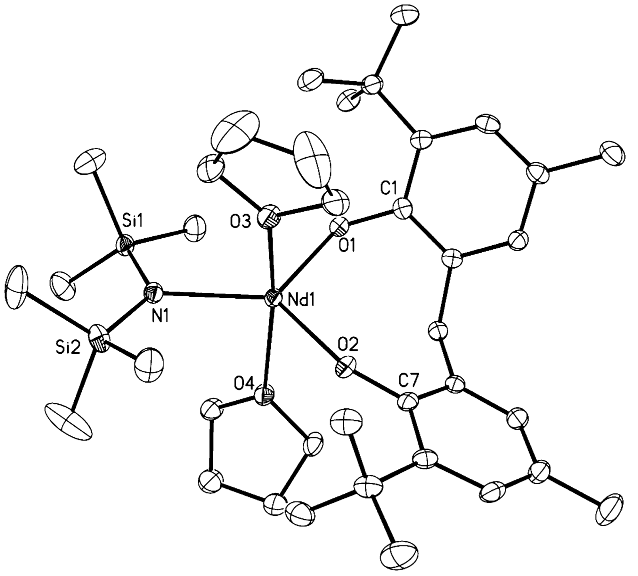

Figure 2. ORTEP diagram of **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd(1)−O(1) 2.214(2), Nd(1)−O(2) 2.187(2), Nd(1)−N(1) 2.352(3), Nd(1)−Si(1) 3.4338(9); O(2)−Nd(1)−O(1) 104.28(8), O(2)−Nd(1)−N(1) 131.07(9), O(1)−Nd(1)−N(1) 124.50(8), O(3)−Nd(1)−O(4) 163.56(8).

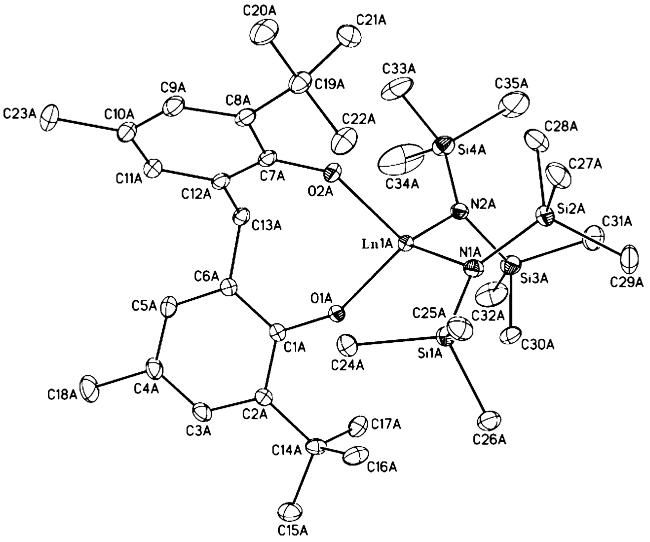

Figure 3. Molecular structure of [Li(THF)$_4$][(MBMP)Ln{N(TMS)$_2$}$_2$] (Ln = Nd (**5**), Yb (**6**)). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) (with data for **6** in parentheses): Ln(1A)−O(1A) 2.211(3) [2.100(3)], Ln(1A)−O(2A) 2.180(3) [2.074(3)], Ln(1A)−N(1A) 2.382(3) [2.238(4)], Ln(1A)−N(2A) 2.361(3) [2.214(4)], Ln(1A)−Si(3A) 3.3821(14) [3.2982(16)]; O(2A)−Ln(1A)−O(1A) 97.15(10) [101.18(13)], O(2A)−Ln(1A)−N(2A) 115.92(11) [114.51(14)], O(1A)−Ln(1A)−N(2A) 102.26(12) [101.91(14)], O(2A)−Ln(1A)−N(1A) 101.99(11) [101.34(14)], O(1A)−Ln(1A)−N(1A) 121.12(11) [122.35(13)], N(2A)−Ln(1A)−N(1A) 117.27(12) [115.20(15)].

accordance with the corresponding bond lengths observed in complexes [(MBMP)Ln(μ-O^{i}Pr)(THF)$_2$]$_2$ (2.215(5) for the neodymium complex; 2.120(3) Å for the ytterbium complex).[2b] The averaged Ln−N bond lengths of 2.371(3) in **5** and 2.226(4) in **6** are comparable with the corresponding values in **3** (2.352(3)), and (C$_5$Me$_5$)$_2$YbNPh$_2$ (2.216(5)),[13] DanipYb[N(SiMe$_3$)$_2$] (2.241(5)) and DanipYb[N(SiHMe$_2$)$_2$]$_2$ (2.209(2) Å) (Danip = 2,6-di(*o*-anisol)phenyl).[14]

Reactions of Lanthanide Amido Complexes with Diisopropyl Carbodiimide. The reactivity of lanthanocene amides with small molecules has been investigated, and these

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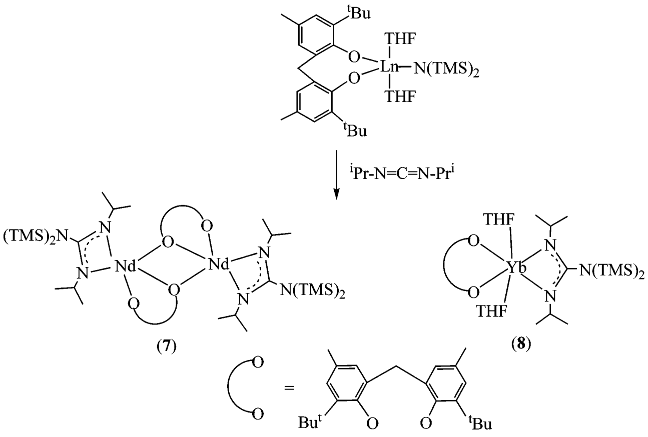
Scheme 2



complexes can activate a number of small molecules, such as CO,[15] CO_2,[16] RNCO,[16b,17] PhNCS,[17d,18] CS_2,[18a] carbodiimides,[17d,18b,19] and nitriles,[16b,20] etc. In contrast, the reactivity of non-cyclopentadienyl lanthanide amido complexes,[21,22] especially the bridged bis(phenolate) lanthanide amido complexes with small molecules, is rarely studied. Recently, insertion reactions of carbodiimide into the Ln−N bond have attracted considerable attention because it provides a convenient method for the synthesis of lanthanide guanidinate complexes.[17d,18b,19,22] To explore the effect of structure on the reactivity of bis(phenolate) lanthanide amido complexes, the insertion reactions of carbodiimide into the Ln−N bonds of the neutral and anionic bis(phenolate) lanthanide amides were investigated. When *N*,*N′*-diisopropylcarbodiimide was added to a THF solution of neutral lanthanide amido **3** and **4** at room temperature, the desired insertion reactions occurred, and the corresponding lanthanide guanidinate complexes $[(\mu\text{-O}-\text{MBMP})\text{Nd}\{(^i\text{PrN})_2\text{CN}(\text{TMS})_2\}]_2$ (**7**) and $(\text{MBMP})\text{Yb}[(^i\text{PrN})_2\text{CN}(\text{TMS})_2](\text{THF})_2$ (**8**) were obtained in moderate isolated yields as shown in Scheme 2. The compositions of **7** and **8** were confirmed with elemental analysis. In their IR spectra, the N═C═N stretch of the parent carbodiimide (2117 cm^{-1}) disappears, and the C═N stretch at approximately 1650 cm^{-1} is observed. These data reflect that π electrons within the double bonds of the N−C−N linkage are delocalized in these complexes.[23] Both **7** and **8** are relatively sensitive to air and moisture. They are readily soluble in THF and toluene but are sparingly soluble in hot *n*-hexane.

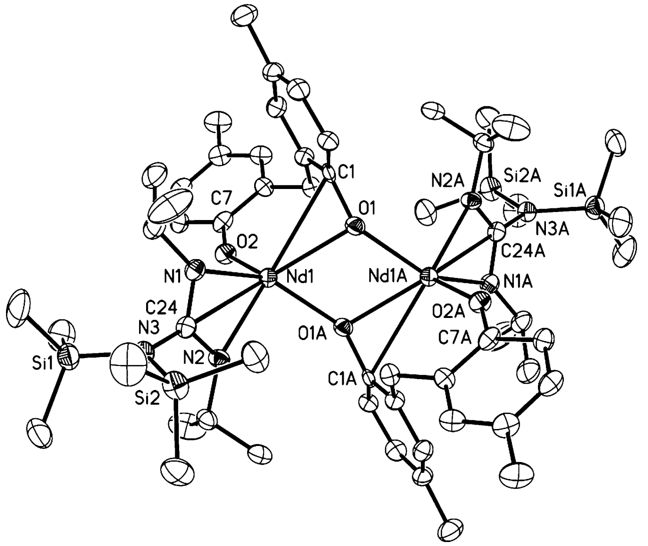


Figure 4. ORTEP diagram of **7** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd(1)−O(1) 2.444(4), Nd(1)−O(2) 2.154(4), Nd(1)−O(1A) 2.368(4), Nd(1)−N(1) 2.427(5), Nd(1)−N(2) 2.460(5), Nd(1)−C(24) 2.889(7), Nd(1)−C(1) 2.919(6); O(2)−Nd(1)−O(1) 112.26(16), O(1A)−Nd(1)−O(1) 69.04(16), N(1)−Nd(1)−N(2) 55.03(18), O(1A)−Nd(1)−O(1) 69.04(16), Nd(1A)−O(1)−Nd(1) 110.96(16), C(1)−O(1)−Nd(1) 94.5(3), C(7)−O(2)−Nd(1) 148.6(4).

The molecular structural diagram of **7** is shown in Figure 4 with its selected bond lengths and bond angles. **7** has an unsolvated centrosymmetric dimeric structure, in which two neodymium atoms were linked by two oxygen atoms from two MBMP groups. Each neodymium atom is bound to three oxygen atoms of two bis(phenolate) ligands and two nitrogen atoms and one carbon atom from the guanidinate ligand. In addition, one carbon atom [C(1)] from one arene ring of the bis(phenolate) ligands is also coordinated to the neodymium atom. Thus, the central metal is seven-coordinated, and the coordination geometry can be described as a distorted tetrahedron when the guanidinate ligand and the phenolate group containing O(1) and C(1) are considered to occupy one coordination site, respectively.

The terminal Nd−O(Ar) bond length of 2.154(4) Å is in accordance with those observed in **1**, **3**, and **5**. Two phenoxo-O atoms are unsymmetrically coordinated to the central metal atoms with a deviation of about 0.06 Å. As expected, the bridging Nd−O(Ar) bond lengths in this complex are larger than those of the terminal ones. The Nd−N bond lengths of 2.427(5) and 2.460(5) Å are similar to the values reported for $[(\text{SiMe}_3)_2\text{NC}(\text{N}^i\text{Pr})_2]\text{Nd}(\mu\text{-Me})_2\text{Li}$-

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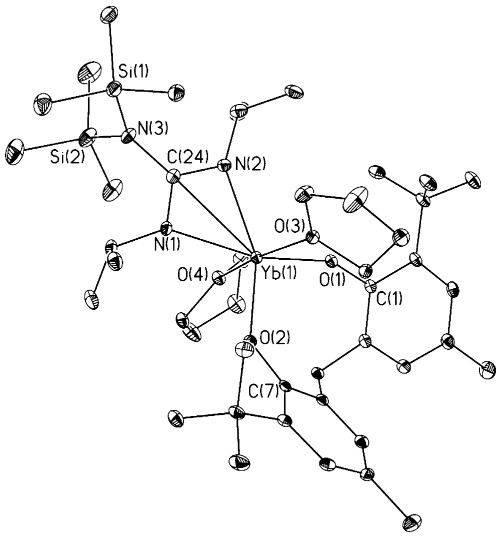
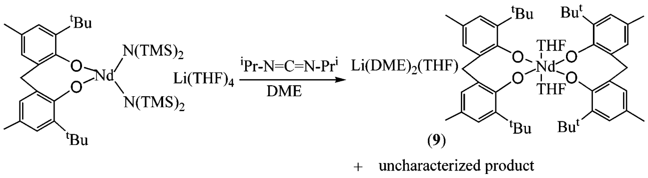


Figure 5. ORTEP diagram of **8** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Yb(1)−O(1) 2.117(3), Yb(1)−O(2) 2.121(3), Yb(1)−N(1) 2.357(4), Yb(1)−N(2) 2.365(4), Yb(1)−C(24) 2.797(6); O(1)−Yb(1)−O(2) 100.59(13), O(2)−Yb(1)−N(1) 96.06(15), N(1)−Yb(1)−N(2) 56.33(15), O(1)−Yb(1)−N(2) 107.48(15), O(3)−Yb(1)−O(4) 170.16(13).

Scheme 3



(TMEDA)(2.476(7) to 2.523(6))[24] and [Nd{$Ph_2NC(NCy)_2$}$_3$](2.464(4) to 2.494(4) Å),[22] when the effect of the coordination number on the effective ionic radius is considered. The Nd−C(24) bond length of 2.889(7) is comparable well with the lanthanide guanidinate complexes mentioned above (2.931(7) and 2.885(8) Å, respectively). It is worth noting that there is a strong π interaction of one carbon atom of the arene ring with the neodymium atom. The Nd−C(1) bond length of 2.919(6) is apparently lower than the Nd−C contact observed in [(MBMP)Nd(μ-O^{i}Pr)$(THF)_2$]$_2$ (3.101(7) Å)[2b] and compares well with those observed in neutral arene neodymium complexes Nd(η^6-C_6H_6)$(AlCl_4)_3$ (2.933(18)),[25a] Nd(η^6-C_6H_5Me)$(AlCl_4)_3$ (2.926(5)),[25b] and Nd(η^6-1,3,5-$C_6H_3Me_3$)$(AlCl_4)_3$ (2.916(9) Å),[25c] in which the Nd−C π interaction was considered to exist unambiguously. Associated with the existence of the π interaction, the Nd−O(1)−C(1) angle of 94.5(3) is apparently smaller than the Nd−O(2)−C(7) angle (145.8(4)°).

An ORTEP diagram depicting the molecular structure of **8** is shown in Figure 5 with the selected bond distances and angles. **8** has a solvated monomeric structure in the solid state. The ytterbium atom is bound to two oxygen atoms of the bis(phenolate) ligands, two nitrogen atoms, one carbon atom from the guanidinate ligand, and two oxygen atoms from two THF molecules. There is no π interaction between the ytterbium atom and the arene rings of the bis(phenolate) ligands. The central metal atom is seven-coordinated to form a distorted trigonal bipyramid, when the η^2-guanidinate ligand is considered to occupy one coordination site. The average Yb−O(Ar) bond length of 2.119(3) Å is slightly larger than those corresponding values in **2** and **4**. The Yb−N bond lengths of 2.357(5) and 2.365(4) Å are comparable well with those in **7** when the difference in ionic radius is considered.

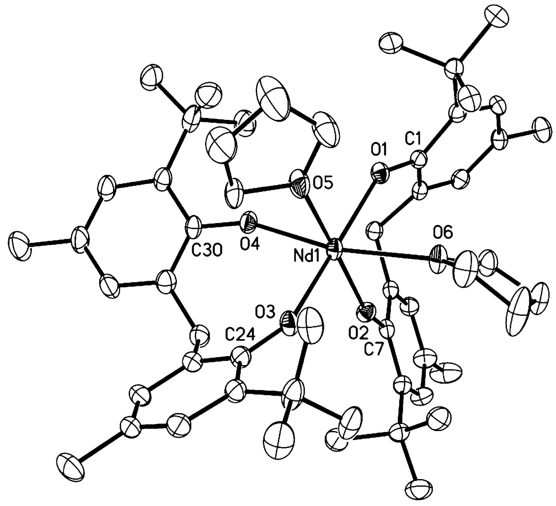


Figure 6. ORTEP diagram of the anion of **9** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd(1)−O(1) 2.275(4), Nd(1)−O(2) 2.229(4), Nd(1)−O(3) 2.266(4), Nd(1)−O(4) 2.223(4); O(4)−Nd(1)−O(2) 102.86(14), O(6)−Nd(1)−O(5) 87.63(13), O(3)−Nd(1)−O(1) 173.07(14), O(4)−Nd(1)−O(5) 83.75(14), O(2)−Nd(1)−O(6) 86.69(14).

Reaction of anionic lanthanide amido **5** with carbodiimide, however, gave an unexpected -ate complex [Li$(DME)_2$(THF)][$(MBMP)_2$Nd$(THF)_2$] (**9**) in moderate yield as shown in Scheme 3. **9** was well characterized; further single-crystal structure determination revealed that it has a discrete ion-pair structure (below). The formation of **9** revealed that the ligand-redistribution reaction occurred. Attempts to isolate the other products from this solution were unsuccessful so far. The analogous rearrangement reaction was reported previously by Zhou et al. The reaction of *N,N′*-diisopropylcarbodiimide with (C_5H_5)Y(N^{i}Pr$_2$)$_2$(THF)$_x$ in a 2:1 molar ratio gave the homoleptic yttrium guanidinate complex Y[^{i}PrNC(N^{i}Pr$_2$)N^{i}Pr]$_3$, and $(C_5H_5)_2$Y[^{i}PrNC(N^{i}Pr$_2$)N^{i}Pr], which was postulated to undergo a diinsertion intermediate (C_5H_5)Y[^{i}PrNC(N^{i}Pr$_2$)N^{i}Pr]$_2$.[19a]

9 is composed of a discrete six-coordinate [$(MBMP)_2$Nd$(THF)_2$]$^-$ anion and a [Li$(DME)_2$(THF)]$^+$ cation. The structure of the anion is shown in Figure 6, with the selected bond lengths and angles. In the cation, the lithium atom is coordinated with five oxygen atoms from two DME molecules and one THF molecule to form a slightly distorted trigonal bipyramidal geometry, which is different from those in **5** and **6**. In the anion, the coordination geometry around the neodymium atom is identical to that in [Na$(DME)_2$-

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Table 3. Polymerization of ϵ-Caprolactone by **3**−**6**[a]

entry	initiator	[M]/[I]	Time	Tp(°C)	Yield(%)[b]	$M_n(10^{-4})$[c]	PDI[c]
1	**3**	300	15 min	50	100	11.03	1.33
2	**3**	400	15 min	25	70	9.68	1.31
3	**3**	400	10 min	50	86	10.67	1.17
4	**3**	500	15 min	25	36	5.95	1.20
5	**3**	500	15 min	50	88	13.07	1.19
6	**4**	200	1h	25	22	4.66	1.40
7	**4**	400	4h	50	44	1.54	1.32
8	**4**	400	10.5h	50	68	2.59	1.36
9	**5**	300	5 min	25	86	3.96	1.18
10	**5**	300	15 min	50	100	9.81	1.67
11	**5**	500	15 min	25	88	10.13	1.24
12	**5**	500	15 min	50	100	11.68	1.84
13	**6**	200	30 min	25	57	4.68	1.78
14	**6**	300	15 min	25	30	5.83	1.69
15	**6**	300	15 min	50	80	7.99	1.70
16	**6**	400	10 min	25	16		
17	**6**	400	10 min	50	46	12.13	1.85

[a] Polymerization conditions: toluene as solvent, $V_{sol.}/V_{[M]} = 4:1$. [b] Isolated yield. [c] Determined by GPC analysis in THF calibrated with standard poly(styrene).

$(THF)_2][(MBMP)_2Yb(THF)_2]$.[2c] The neodymium atom is located in the center of an octahedron comprised by two $MBMP^{2-}$ groups and two THF molecules.

The Nd−O(Ar) bond lengths range from 2.223(4) to 2.275(4), giving an average of 2.248(4) Å, which is slightly larger than the terminal Nd−O(Ar) bond lengths in **1** and **3**, but is comparable with the corresponding value in $[Na(DME)_2(THF)_2][(MBMP)_2Yb(THF)_2]$ (2.140(6) Å),[2c] when the difference in ionic radius is considered. The bite angles of O−Nd−O in **9** are 93.19(13) and 91.07(14)°, respectively, which are comparable with those in **1** and **3**.

Ring-Opening Polymerization of ϵ-Caprolactone by 3−6. In recent years, the application of structurally well-defined organometallic and coordination complexes as initiators for the synthesis of aliphatic polyesters, such as poly(ϵ-caprolactone) (PCL) and poly(lactide) (PLA), via the ring-opening polymerization of lactones/lactides and functionally related compounds has received considerable attention because these catalyst systems afford the possibility of understanding the catalyst structure/reactivity relationships.[26] To understand the effect of bis(phenolate) ligands on the polymerization activity and controllability, the catalytic behavior of methylene-linked bis(phenolate) lanthanide amido complexes **3**−**6** for the ring-opening polymerization of ϵ-caprolactone was examined.

The polymerization results are summarized in Table 3. It can be seen that all of the lanthanide amido complexes can initiate effectively ϵ-caprolactone polymerization, and all of the polymers obtained with these initiators have high molecular weights and relatively narrow molecular weight distributions (PDIs). As expected, the polymerizations at higher temperature were faster than those at room temperature. However, the polymerization temperature affects the reaction rate but not the molecular weights and PDIs of the polymers obtained under the same polymerization conditions, using neutral lanthanide amides **3** and **4** as initiators; all of the polymerizations give polymers with small PDIs at room temperature or at 50 °C. The polymerization temperature affects not only the reaction rate but also the PDIs of the resulting polymers using the anionic lanthanide amide **5** for polymerization. The PDIs are small (<1.30) when the polymerizations are conducted at room temperature, whereas the PDIs become larger (>1.60) when the polymerizations are carried out at 50 °C. But the PDIs of the polymers obtained using **6** as initiators are relatively larger whenever the polymerizations are conducted at room temperature or at 50 °C. The reason causing this difference is still unclear.

The anionic bis(phenolate) lanthanide amides showed higher activity for polymerization than the neutral ones. Using **5** as the initiator, the yield reaches 88% in 15 min at room temperature when the molar ratio of monomer to initiator ($[M_0]/[I_0]$) is 500, whereas the yield is 36% using **3** as the initiator under the same polymerization conditions (Entries 11, 4). All of the GPC curves of the resulting polymers are unimodal. These results clearly indicate that the anionic lanthanide complexes were really used as single-component initiators in ϵ-caprolactone polymerization. It is possible that the increased activity of the anionic lanthanide complexes stems from the cooperation of the anion and the cation, although the reaction mechanism is unclear. Actually, a number of anionic lanthanide complexes were found to show unique activity for the polymerization of some polar and nonpolar monomers, whereas the corresponding neutral lanthanide complexes showed very low activity, and, in some cases, were even inactive for these polymerizations.[27]

The central metal ion has a profound effect on the polymerization, no matter what anionic or the neutral lanthanide amides were used as initiators. Using neodymium amido complex **5** as the initiator, the yield was 88% when the molar ratio of monomer to initiator is 500 (Entry 11), whereas it was 30% using ytterbium amido complex **6** for polymerization, even when the molar ratio of monomer to initiator decreases to 300 (Entry 14) under the same polymerization temperature. The active trend is consistent with the increasing order of their ionic radii, which is consistent with those observed in the methylene-linked bis(phenolate) lanthanide alkoxide systems.[2b]

The neutral methylene-linked bis(phenolate) lanthanide amides showed slightly lower activity for this polymerization than the corresponding lanthanide alkoxides. For instance, the yield was 86% (Entry 3) using **3** as the initiator and 100% using the corresponding neodymium isopropoxide as the initiator,[28] under the same polymerization conditions. But

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all of the polymers obtained by these initiators have small PDIs (<1.40), which indicated that the neutral methylene-linked bis(phenolate) lanthanide derivatives have good controllability for ϵ-caprolactone polymerization. However, the activities of these neutral lanthanide amides are apparently lower than those of the amine bis(phenolate) lanthanide amides.[1e] Using ytterbium amido complex **4** for polymerization, the yield reached 22% in 1 h at 25 °C, when the molar ratio of monomer to the initiator is 200 (entry 6), whereas when using the amine bis(phenolate) ytterbium amide as the initiator, the polymerization completed within 1 min at 25 °C, even when the molar ratio of monomer to initiator increases to 2000. But the polymers obtained for the amine bis(phenolate) lanthanide amides have apparently larger PDIs (>1.70).[1e] These results indicated that the methylene-linked bis(phenolate) lanthanide amides have better controllability for this polymerization than the amine bis(phenolate) lanthanide amides. In comparison with those results initiated by the methylene-linked bis(phenolate) lanthanide alkoxides[2b] and amine bis(phenolate) lanthanide amides,[1e] ancillary ligands have a profound effect on the activity and the controllability for ϵ-caprolactone polymerization, whereas the active groups have a relatively minor effect.

Conclusion

In summary, the methylene-linked bis(phenolate) lanthanide chlorides can be conveniently synthesized by amine elimination reactions, and these chlorides were found to be useful precursors for the synthesis of the corresponding lanthanide amides. The first example was provided that the neutral and anionic lanthanide derivatives stabilized by the same ancillary ligand can be synthesized in a controlled manner by general metathesis reactions by turning of the molar ratio of the reagents. Reactions of the methylene-linked bis(phenolate) lanthanide chlorides with 2 equiv of sodium amide gave the neutral lanthanide amides, whereas the reactions with 4 equiv of lithium amide gave the anionic products. The neutral and anionic bis(phenolate) lanthanide amides showed different reactivity. The neutral lanthanide amides reacted with carbodiimide to give the normal insertion products, whereas the similar reaction of the anionic lanthanide amide gave the ligand-redistributed products. The anionic lanthanide amides are more active than the neutral ones for ϵ-caprolactone polymerization. For the bridged bis(phenolate) lanthanide derivatives, the ancillary ligands dominate the activity and the controllability for ϵ-caprolactone polymerization, whereas the active groups play a minor role. The presence of donor atom(s) on the linker of the bis(phenolate) lanthanide complexes increases the activity for ϵ-caprolactone polymerization but decreases the controllability.

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Supporting Information Available: Crystallographic data for **1**−**3** and **5**−**9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Although we previously reported that 100% yield can be reached in 1 h using methylene-linked bis(phenolate) neodymium isopropoxide as an initiator,[2b] the polymerization is now found to complete in 10 min.