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Synthesis, Reactivity, and Structural Characterization of Sodium and Ytterbium Complexes Containing New Imidazolidine-Bridged Bis(phenolato) Ligands

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A new imidazolidine-bridged bis(phenol) $[ONNO]H_2$ ($[ONNO]H_2$ = 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)-imidazolidine) was prepared in relatively high yield by Mannish reaction of 2,4-di-*tert*-butylphenol, formaldehyde, and ethylenediamine in a 2:3:1 molar ratio. Reaction of the bis(phenol) with NaH in THF, after workup, afforded the sodium bis(phenolate) $\{[ONNO]Na_2(THF)_2\}_2 \cdot 2THF$ (**1**) as a dimeric tetranuclear complex in an almost quantitative yield. Reaction of $YbCl_3$ with complex **1** in a 2:1 molar ratio in THF, in the presence of HMPA, produced the desired bis(phenolate) ytterbium dichloride as bimetallic complex $[ONNO]\{YbCl_2(HMPA)\}_2 \cdot 2.5C_7H_8$ (**2**). Complex **2** can be used as a precursor for the synthesis of ytterbium derivatives by salt metathesis reactions. Reaction of complex **2** with NaO^iPr in a 1:2 molar ratio in THF led to the formation of bimetallic alkoxide $[ONNO]\{Yb(\mu\text{-}O^i\text{-}Pr)Cl(HMPA)\}_2 \cdot THF$ (**3**). However, the residual chlorine atoms in complex **3** are inactive for the further substituted reaction. Further study revealed that the bulkiness of the reagent has profound effect on the outcome of the reaction. Complex **2** reacted with bulky NaOAr (ArO = 2,6-di-*tert*-butyl-4-methylphenoxo) or $NaNPh_2$ in a 1:2 molar ratio under the same reaction conditions, after workup, to give the ligand redistributed products, $(ArO)_2YbCl(HMPA)_2$ (**4**) and $[ONNO]YbCl(HMPA)_2$ (**5**) for the former and complexes **5** and $(Ph_2N)_2YbCl(HMPA)_2$ (**6**) for the latter. If the molar ratio of complex **2** to $NaNPh_2$ decreased to 1:4, the expected ligand redistributed products $[ONNO]YbNPh_2(HMPA)$ (**7**) and $(Ph_2N)_3Yb(HMPA)_2 \cdot C_7H_8$ (**8**) can be isolated in high yields. All of the complexes were well characterized, and the definitive molecular structures of complexes **1**–**4**, **7**, and **8** were provided by single-crystal X-ray analysis.

Introduction

In recent years, bridged bis(phenolate) ligands have received considerable attention in organolanthanide chemistry because they are easily available, tunable, and even potentially recyclable, which thus 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 exhibit exciting reactivity. 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 carbon-bridged bis(phenolate) lanthanide alkoxides can polymerize ϵ-caprolactone in a controllable manner,[2b,e] and the divalent ytterbium complex stabilized by amine bis(phenolate) ligands,

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as a single electron-transfer reagent, can activate some small molecules, such as PhNCO and PhC≡CH, etc.[1l]

The presence of a heteroatom on the bridged bis(phenolate) ligands seems to have significant effect on the reactivity of the corresponding metal complexes. The titanium complexes containing sulfur- or tellurium-bridged bis(phenolate) ligands were reported to show distinctively high activity for the polymerization of ethylene and propylene upon activation with methylaluminoxane (MAO) in comparison with those of the corresponding methylene-bridged bis(phenolate) and the similar 2,2′-diphenolate titanium complexes.[4] A theoretical study revealed that the coordination of the sulfur or tellurium atom was essential to reduce the activation energy for olefin insertion into a metal−carbon bond.[5] Our previous studies also revealed that the lanthanide complexes supported by the amine bis(phenolate) ligands showed higher catalytic activities for ϵ-caprolactone polymerization than the methylene-linked ones.[1e,2b] This encouraged us to systematically investigate the effect of heteroatoms of the ancillary ligands on the reactivity of the corresponding lanthanide complexes.

In general, the metathesis reaction of bis(cyclopentadienyl) lanthanide halides with lithium alkyls or amides is a convenient method for the synthesis of the lanthanocene derivatives.[6] However, this general rule is problematic for the synthesis of non-cyclopentadienyl lanthanide complexes, due to the formation of salt inclusion lanthanide complexes.[1k] To date, most of the lanthanide complexes which have the general formula LLnX, where L = dianionic bridged bis(phenolate) ligands and X = a monoanionic active group, were synthesized by 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 addition to ligand exchange pathways, we recently reported the successful synthesis of neutral ytterbium (III) amine bis(phenolate) complexes by direct metathesis reaction.[1e] It is interesting to know whether this is a special case. Therefore, we intend to expand this synthetic method to other bis(phenolate) ligand systems. In this paper, a new imidazolidine-bridged bis(phenol) was prepared, and a series of lanthanide derivatives supported by this ligand system were synthesized by direct salt metathesis reaction. Here we report these results.

Experimental Section

All reagents are reagent grade and commercially available and used as received unless otherwise noted. All manipulations were performed under argon, using the standard Schlenk techniques. THF, toluene, and hexane were distilled from sodium benzophenone ketyl before use. HMPA was dried over CaH_2 for 4 days and distilled under reduced pressure. (***Caution!*** *HMPA is a cancer suspect agent and should be handled with discretion*.) Isopropanol was dried with a small amount of sodium and distilled before use. Lanthanide metal analysis was performed by EDTA titration with an xylenol orange indicator and a hexamine buffer,[7] and chloride analysis was carried out using the Volhard method. 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. ^{1}H NMR spectra were obtained on an INOVA-400 MHz apparatus. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

Synthesis of Ligand [ONNO]H_2. 2,4-Di-*tert*-butylphenol (4.12 g, 20.0 mmol) was dissolved in 50 mL methanol, and to this solution was added aqueous formaldehyde solution (4.11 mL, 50.0 mmol) and ethylenediamine (0.67 mL, 10.0 mmol). The mixture was stirred overnight and refluxed in methanol, and a white precipitate appeared during this period. After the reaction mixture was cooled to room temperature, the product was collected by filtration and finally recrystallized from hot petroleum ether (3.31 g, 65%). Mp: 184.1−184.5 °C. Anal. Calcd for $C_{33}H_{52}N_2O_2$: C, 77.90; H, 10.30; N, 5.50%. Found: C, 78.06; H, 10.44; N, 5.38%. IR (KBr, cm^{-1}): 3167 (br, m), 2955 (s), 2905 (s), 2866 (s), 2827 (s), 1770 (w), 1608 (m), 1481 (s), 1389 (s), 1362 (s), 1304 (s), 1234 (s), 1087 (m), 880 (m). ^{1}H NMR (400 Hz, $CDCl_3$): 10.73 (br, 2H, OH), 7.22 (s, 2H, Ph), 6.83 (s, 2H, Ph), 3.89 (s, 4H, CH_2), 3.52 (s, 2H, imidazolidine ring), 2.99 (br, 4H, imidazolidine ring), 1.42 (s, 18H, ^{t}Bu), 1.28 (s, 18H, ^{t}Bu). HRMS, *m*/*z*: 508.3871 (M^+).

Synthesis of $\{$[ONNO]$Na_2(THF)_2\}_2\cdot 2THF$ (1). To a stirred suspension of NaH (1.5 equiv) in THF, the solution of [ONNO]H_2 (5.08 g, 10.0 mmol) in THF was added dropwise. The mixture was continuously stirred at room temperature overnight and then centrifuged. The precipitate was washed with hot THF twice, and the decantate was combined and concentrated. Colorless crystals were obtained from the concentrated THF solution (7.61 g, 99%). Mp: 219−221 °C. Anal. Calcd for $C_{90}H_{148}N_4Na_4O_{10}$: C, 70.28; H, 9.70; N, 3.64%. Found: C, 70.16; H, 9.57; N, 3.48%. IR (KBr, cm^{-1}): 2956 (s), 2871 (s), 1775 (w), 1652 (w), 1605 (m), 1459 (s), 1389 (m), 1358 (m), 1297 (w), 1235 (m), 1165 (w), 880 (m). ^{1}H NMR (400 Hz, $CDCl_3$): 7.21 (s, 2H, Ph), 6.82 (s, 2H, Ph),

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Table 1. Crystallographic Data for Complexes **1**−**4**, **7**, and **8**

compd	**1**	**2**	**3**	**4**	**7**	**8**
formula	$C_{90}H_{148}N_4Na_4O_{10}$	$C_{62.50}H_{106}Cl_4N_8O_4P_2Yb_2$	$C_{55}H_{108}Cl_2N_8O_7P_2Yb_2$	$C_{42}H_{82}ClN_6O_4P_2Yb$	$C_{51}H_{78}N_6O_3PYb$	$C_{55}H_{74}N_9O_2P_2Yb$
fw	1538.08	1583.37	1472.41	1005.57	1027.20	1128.21
T(K)	193(2)	193(2)	173(2)	193(2)	153(2)	173(2)
cryst syst	triclinic	Monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	*Pbcn*	*Pbca*	$P2_1/c$
a (Å)	10.4123(18)	15.9447(17)	17.4291(11)	32.547(2)	14.1000(5)	16.5515(13)
b (Å)	15.5300(18)	24.683(3)	17.1060(11)	18.1550(8)	27.5165(11)	16.2383(12)
c (Å)	15.9655(19)	18.6684(19)	23.4174(16)	16.7632(10)	54.844(2)	20.9858(17)
α (deg)	66.699(11)					
β (deg)	85.856(16)	94.481(3)	91.022(2)			102.783(2)
γ (deg)	78.656(15)					
V (Å^3)	2324.7(6)	7324.7(13)	6980.6(8)	9905.3(10)	21278.6(14)	5500.5(7)
Z	1	4	4	8	16	4
D_{calcd} (g cm^{-3})	1.099	1.436	1.401	1.349	1.283	1.806
μ (mm^{-1})	0.086	2.774	2.834	2.050	1.832	2.774
F(000)	840	3228	3016	4200	8560	2332
cryst size (mm)	0.40 × 0.28 × 0.22	0.30 × 0.23 × 0.14	0.50 × 0.44 × 0.30	0.32 × 0.30 × 0.29	0.50 × 0.30 × 0.12	0.48 × 0.30 × 0.29
θ_{max} (deg)	25.3	25.35	25.35	25.35	25.35	25.35
collected reflns	23344	69167	65653	89927	113177	52864
unique reflections	8467	13390	12742	9052	19127	10051
observed reflns [$I > 2.0\sigma(I)$]	5875	11062	11616	7971	15937	8589
no. of variables	500	759	640	532	1154	636
GOF	1.103	1.178	1.135	1.225	1.141	1.080
R	0.0817	0.0723	0.0596	0.0424	0.0621	0.0664
wR	0.2042	0.1732	0.1382	0.0792	0.1226	0.1732

3.87 (s, 4H, CH_2), 3.72 (br, 12H, THF), 3.50 (s, 2H, imidazolidine ring), 2.98 (br, 4H, imidazolidine ring), 1.84 (br, 12H, THF), 1.40 (s, 18H, ^{t}Bu), 1.28 (s, 18H, ^{t}Bu).

Synthesis of [ONNO]{$YbCl_2$(HMPA)}$_2$·2.5C_7H_8 (2). To a slurry of anhydrous $YbCl_3$ (1.40 g, 5.0 mmol) in THF was added a hot solution of complex **1** (1.92 g, 1.25 mmol) in THF. The mixture was stirred at 50 °C for about 8 h, and a red precipitate formed gradually. After the reaction mixture was cooled to room temperature, 0.87 mL of HMPA was added dropwise to the stirred suspension. The color of the system turned slowly yellow, and a colorless gel-like matter appeared at the same time. The system was continuously stirred at room temperature for another 2 h, and the precipitate was removed from the reaction mixture by centrifugation. THF was completely evaporated in vacuum, and toluene was added. Yellow crystals were obtained from the concentrated toluene solution at −10 °C in a few days (2.65 g, 67%). Mp: 245−247 °C. Anal. Calcd for $C_{62.50}H_{106}Cl_4N_8O_4P_2Yb_2$: C, 47.41; H, 6.75; N, 7.07; Cl, 8.96; Yb, 21.86%. Found: C, 47.16; H, 6.54; N, 6.88; Cl, 8.74; Yb, 21.69%. IR (KBr, cm^{-1}): 2953 (s), 2921 (s), 2856 (s), 1743 (w), 1650 (w), 1604 (m), 1463 (s), 1369 (m), 1356 (m), 1287 (w), 1235 (m), 1165 (w), 850 (m).

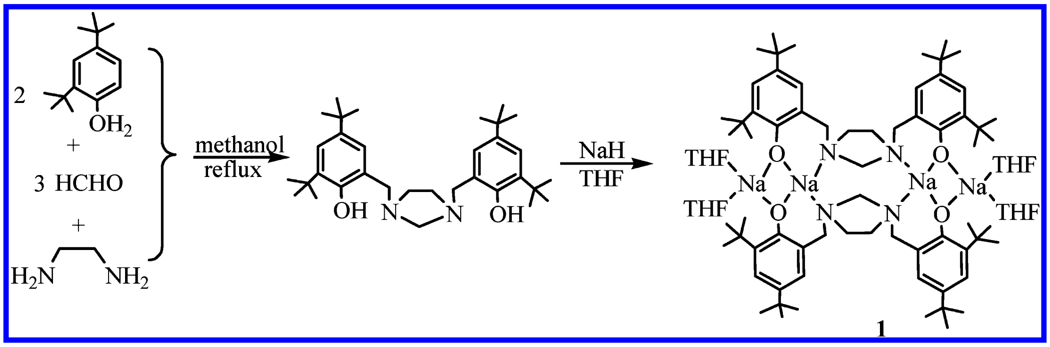
Synthesis of [ONNO]{Yb(μ-O^{i}Pr)Cl(HMPA)}$_2$·THF (3). The crystalline solid of complex **2** (3.65 g, 2.31 mmol) was dissolved in THF, and the hot THF solution of NaO^{i}Pr (0.38 g, 4.61 mmol) was added. The color of the reaction mixture turned lemon-yellow, and the gel-like precipitate formed immediately. The reaction mixture was stirred overnight at room temperature, and the precipitate was removed by centrifugation. The solution was concentrated to about 8 mL, and a colorless crystal-like solid formed in 2 days (2.82 g, 83%). Mp: 223−225 °C. Anal. Calcd for $C_{55}H_{108}Cl_2N_8O_7P_2Yb_2$: C, 44.87; H, 7.39; N, 7.61; Cl, 4.82; Yb, 23.50%. Found: C, 44.57; H, 7.14; N, 7.38; Cl, 4.65; Yb, 23.22%. IR (KBr, cm^{-1}): 2951 (s), 2920 (s), 2855 (s), 2812 (m), 1736 (w), 1604 (m), 1481 (s), 1442 (s), 1361 (s), 1304 (s), 1238 (s), 1192 (m), 1149 (s), 1068 (m), 991 (s), 841 (m), 756 (s). Crystals suitable for X-ray structure analysis were obtained by the slow cooling of a hot THF solution.

Synthesis of (ArO)$_2$YbCl(HMPA)$_2$ (4) and [ONNO]YbCl(HMPA)$_2$ (5). A THF solution of NaOAr (6.0 mL, 5.30 mmol) was added to the stirred THF solution of complex **2** (4.20 g, 2.65 mmol). The color of the mixture turned from orange to yellow, and a gel-like precipitate was formed immediately. The reaction mixture was stirred at room temperature overnight, and the precipitate was removed by centrifugation. To the solution was added HMPA (0.90 mL), and the mixture was stirred for about an hour. The solvent was evaporated in vacuum, and hot toluene (25 mL) was added. Yellow star-like crystals of complex **4** were obtained in 4 days in 37% yield (1.00 g). Mp: 108−110 °C. Anal. Calcd for $C_{42}H_{82}ClN_6O_4P_2Yb$ (**4**): C, 50.17; H, 8.22; N, 8.35; Cl, 3.53; Yb, 17.21%. Found: C, 49.96; H, 8.06; N, 8.18; Cl, 3.37; Yb, 17.06%. IR (KBr, cm^{-1}): 2955 (s), 2913 (w), 2871 (w), 1731 (w), 1603 (s), 1430 (s), 1389 (m), 1367 (m), 1232 (s), 1153 (s), 1121 (w), 866 (s), 772 (s). After toluene was removed from the mother liquor, hot hexane (30 mL) was added to extract another product. A pale yellow crystalline solid of complex **5** was obtained in 2 days in 18% yield (0.49 g). Mp: 187−189 °C. Anal. Calcd for $C_{45}H_{86}ClN_8O_4P_2Yb$ (**5**): C, 50.34; H, 8.07; N, 10.44; Cl, 3.30; Yb, 16.12%. Found: C, 50.06; H, 7.84; N, 10.28; Cl, 3.13; Yb, 15.98%. IR (KBr, cm^{-1}): 2951 (s), 2919 (s), 2857 (s), 1743 (w), 1652 (w), 1611 (m), 1453 (s), 1389 (m), 1357 (m), 1285 (w), 1233 (m), 1158 (w), 854 (m).

Synthesis of (Ph_2N)$_2$YbCl(HMPA)$_2$ (6). The synthesis of complex **6** was carried out as described for complex **4**, but $NaNPh_2$ (5.68 mL, 4.86 mmol) was used in place of NaOAr. After workup, complex **6** was obtained from the toluene solution in 32% yield (0.71 g). Mp: 211−213 °C. Anal. Calcd for $C_{36}H_{56}ClN_8P_2O_2Yb$: C, 47.87; H, 6.25; N, 12.40; Cl, 3.92; Yb, 19.16%. Found: C, 48.06; H, 6.26; N, 11.98; Cl, 3.63; Yb, 18.87%. IR (KBr, cm^{-1}): 3036 (w), 2952 (s), 2903 (s), 2863 (s), 1734 (w), 1597 (s), 1522 (s), 1491 (s), 1459 (s), 1332 (s), 1244 (w), 1172 (m), 1087 (w), 880 (m), 702 (m), 690 (s). Complex **5** was also isolated from the hexane solution in 23% yield (0.62 g).

Synthesis of [ONNO]YbNPh_2(HMPA) (7) and (Ph_2N)$_3$Yb(HMPA)$_2$·C_7H_8 (8). The synthesis of complexes **7** and **8** was carried out similarly as described for complexes **5** and **6**, but the molar ratio of complex **2** (3.80 g, 2.40 mmol) to $NaNPh_2$ was 1:4. After the NaCl was removed from the reaction mixture, the system was dried in vacuum, and hot hexane (35 mL) was added. Complex

Scheme 1



8 was precipitated immediately as a deep red crystalline solid in 36% yield (0.97 g). Mp: 185−187 °C, Anal. Calcd for $C_{55}H_{74}N_9O_2P_2$-Yb: C, 58.55; H, 6.61; N, 11.17; Yb, 15.34%. Found: C, 55.26; H, 6.35; N, 10.84; Yb, 15.17%. IR (KBr, cm^{-1}): 3035 (w), 2951 (s), 2903 (s), 2862 (s), 1734 (w), 1595 (s), 1523 (s), 1491 (s), 1457 (s), 1332 (s), 1244 (w), 1170 (m), 1087 (w), 881 (m), 702 (m), 691 (s). Complex **7** was obtained as a yellow powder from the concentrated hexane solution in 22% yield (0.54 g). Mp: 257−259 °C. Anal. Calcd for $C_{51}H_{78}N_6O_3PYb$: C, 59.63; H, 7.65; N, 8.18; Yb, 16.85%. Found: C, 59.32; H, 7.36; N, 7.87; Yb, 16.63%. IR (KBr, cm^{-1}): 2958 (s), 2904 (s), 2866 (s), 1739 (w), 1602 (s), 1525 (m), 1472 (s), 1410 (m), 1389 (m), 1362 (m), 1303 (s), 1238 (m), 1029 (m), 879 (m), 748 (s). Crystals suitable for an X-ray crystal structure study were obtained by cooling the hot toluene (for complex **8**) or the hot hexane solution (for complex **7**) in about 2 weeks.

X-ray Crystallography. Suitable single crystals of complexes **1**−**4**, **7**, and **8** 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 ($\lambda = 0.710\ 70$ 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 the non-hydrogen atoms were refined anisotropically. All 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 SHELEXL-97 programs.

Results and Discussion

Synthesis and Characterization of the Ligand and Its Sodium Salt. Mannich reaction is a convenient method to synthesize amine bridged bis(phenol). However, the product of the reaction of phenol, aldehyde, and diamine will be affected by the reagent and the reaction temperature.[8] Kol and co-workers once reported the synthesis of ethylenediamine bridged bis(phenol) by refluxing corresponding reagents in methanol,[9] but our attempts to repeat this reaction failed. A bridged benzoxazine can be obtained in very high yield when the reaction proceeded at about 85 °C (oil bath).[10] Further study revealed that the reaction temperature is a key for the reaction pathway. A new imidazolidine bridged bis(phenol) $[ONNO]H_2$ ($[ONNO]H_2$ = 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)imidazolidine) can be isolated as the major product in about 65% yield when the reaction proceeded at about 66 °C (oil bath) (Scheme 1). This compound is fully characterized by elemental analysis, ^1H NMR, IR, and HRMS.

Reaction of $[ONNO]H_2$ with NaH in THF, after workup, afforded sodium bis(phenolate) $\{[ONNO]Na_2(THF)_2\}_2$ (**1**) in an almost quantitative yield. Complex **1** is well characterized by elemental analysis, IR, and ^1H NMR, and the definitive molecular structure was confirmed by X-ray diffraction to be a dimeric complex. Complex **1** was slightly soluble in THF and toluene and soluble in hot THF.

Lithium and sodium aryloxides are common starting materials for the synthesis of transition metal and lanthanide aryloxides via a transmetalation reaction.[11] In general, these alkali metal aryloxides have polymeric or polynuclear structure, and the steric bulk and electron-donation ability of the ortho-substituent groups have profound effect on their solid-state structures.[12] The molecular structures of alkali metal complexes bearing monoaryloxides have been widely reported,[13] but that of bridged bis(phenolate), especially for sodium, is rather scant.[14] Crystals of complex **1** suitable for X-ray structure determination were obtained from a concentrated THF solution. The selected bond lengths and angles are listed in Table 2. An ORTEP of complex **1** is depicted in Figure 1. Complex **1** has a dimeric tetranuclear structure: two inner sodium atoms are coordinated by two nitrogen atoms from the imidazolidine rings and two oxygen atoms from the aryloxo groups, respectively, whereas two outer sodium atoms are coordinated by two oxygen atoms from the aryloxo groups and two oxygen atoms from two THF molecules. The coordination environment of each of the outer sodium atoms is similar to those in $[(THF)_nLn(MBMP)_2Na(THF)_2]$ (Ln = Nd, Yb; MBMP = 2,2′-methylene-bis(6-*tert*-butyl-4-methyl-phenoxo)).[2c] The coordination number of the sodium atoms is 4, and the coordination geometry of each sodium atom can be best described as a distorted tetrahedron. This coordination geometry is similar to that in $[(4\text{-F-}C_6H_4\text{-}ONa)_6(THF)_8]$[13a] but different from that in $[NaOC_6H_2\text{-}(CH_2\text{-}$

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in Complex **1**

Na(1)−O(2A)	2.226(2)	Na(2)−O(1)	2.183(2)
Na(1)−O(1)	2.247(3)	Na(2)−O(2A)	2.213(3)
Na(1)−N(1)	2.481(3)	Na(2)−O(3)	2.282(3)
Na(1)−N(2A)	2.496(3)	Na(2)−O(4)	2.304(4)
Na(1)−C(17A)	3.069(3)	Na(1)−Na(2)	3.114(2)
Na(1)−C(16)	3.077(3)	Na(1)−Na(1A)	4.035(2)
O(2A)−Na(1)−O(1)	89.55(9)	Na(2)−O(1)−Na(1)	89.34(9)
O(1)−Na(1)−N(1)	87.60(9)	Na(2A)−O(2)−Na(1A)	89.11(9)
O(2A)−Na(1)−N(2A)	86.49(8)	O(1)−Na(2)−O(3)	105.50(11)
N(1)−Na(1)−N(2A)	138.63(9)	O(2A)−Na(2)−O(4)	105.44(12)
O(1)−Na(2)−O(2A)	91.54(9)	O(3)−Na(2)−O(4)	99.08(16)

$NMe_2)_2$-2,6-Me-4$]_4$,[12b] in which the sodium atoms are surrounded by three bridging aryloxide oxygen atoms and two nitrogen atoms from two amino groups.

The Na−O(Ar) bond lengths range from 2.183(2) to 2.247(3) Å, giving an average of 2.217(3) Å, which is close to those Na−O(Ar) bond lengths reported for other sodium aryloxides.[12,13] The Na−N bond lengths of 2.481(3) and 2.496(3) Å are comparable with those in $[NaOC_6H_4{-}(CH_2{-}NMe_2)\text{-}2]_6$.[12a] There are remote π interactions between the sodium atom and the carbon atoms connecting the aryl rings and the imidazolidine rings. The bond lengths of Na(1)−C(16) and Na(1)−C(17A) are 3.077(3) and 3.069(3) Å, respectively, which are comparable with that reported in $(THF)La(OC_6H_3{-}{}^iPr_2\text{-}2,6)_2(\mu\text{-}OC_6H_3{-}{}^iPr_2\text{-}2,6)_2Na(THF)_2$ (3.085(9) Å)[15] but slightly longer than those observed in $(TMEDA)NaC(SiMe_3)_2(SiMe_2Ph)$ (3.026(5) Å).[16]

Synthesis and Reactivity of Ytterbium Complexes. Generally, the lanthanide halides bearing suitable ancillary ligands are considered to be useful precursors for the synthesis of miscellaneous lanthanide derivatives. Therefore, the ytterbium chloride supported by the new imidazolidine-bridged bis(phenolate) ligands was prepared by the normal salt metathesis reaction. Taking into account the bulkiness and the rigidity of the [ONNO] ligand, we intend to synthesize a dinuclear ytterbium dichloride stabilized by this ligand system. Anhydrous $YbCl_3$ reacted with complex **1** in THF in a 4:1 molar ratio at 50 °C for 8 h to give a red precipitate. The red precipitate has sparing solubility even in THF, and the attempts to obtain its crystals suitable for structure determination failed. Because no NaCl precipitated from this reaction system, it is reasonable to postulate that the NaCl is still connected with the ytterbium center. In order to dissociate the NaCl from the precipitate, some chelating solvents such as DME and TMEDA were used, but these attempts were unsuccessful. It was found that the addition of HMPA can solve this problem. After addition of HMPA to the THF suspension of the precipitate, the red precipitate disappeared gradually, and the color of the solution turned yellow. Meanwhile, NaCl precipitated from the reaction system. After workup, complex **2** was isolated from the concentrated toluene solution as yellow crystals in a good yield. Elemental analysis results of complex **2** agree with that of a dinuclear structure with only one-half of the [ONNO] ligand per ytterbium with a formula corresponding to $[ONNO]\{YbCl_2(HMPA)\}_2$, which was confirmed by X-ray structure determination as shown in Scheme 2. Complex **2** has good solubility in THF and toluene and is sensitive to air and moisture.

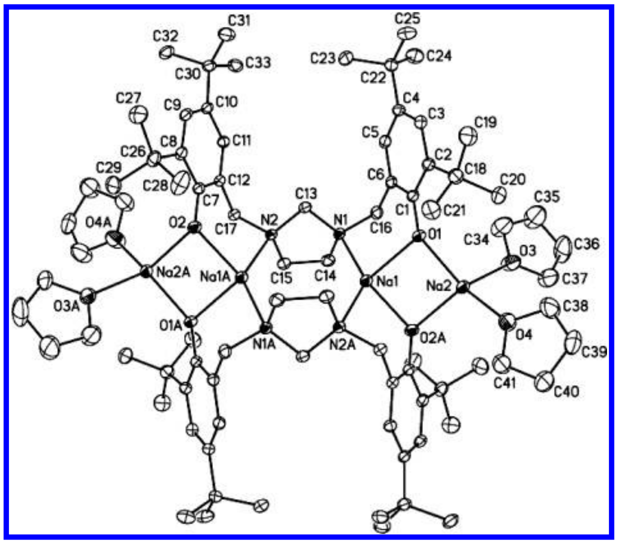

Figure 1. ORTEP diagram of complex **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Few examples are available of bridged bis(phenolate) lanthanide systems where salt metathesis routes are successful in the synthesis of lanthanide derivatives from halides. Mountford and co-workers previously reported that the yttrium and scandium chlorides supported by the tetradentate diamino-bis(phenolate) ligands $O_2{}^{tBu}NN'$ $[O_2{}^{tBu}NN' = (2\text{-}C_5H_4N)CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2{}^tBu_2\text{-}3,5)_2\}]$ were inactive for many halide substitution reactions.[1f] We had found that the ytterbium chloride bearing amine bis(phenolate) ligands is a useful precursor for the synthesis of ytterbium alkyls and amides by general metathesis reactions.[1g] In order to elucidate the reactivity of the Yb−Cl bonds in complex **2**, the chloride substituted reactions were employed. Complex **2** reacted with sodium isopropoxide in a 2:1 molar ratio in THF, after workup, to give complex **3** as colorless crystals. Elemental analysis results are consistent with that of a dinuclear structure. The definitive molecular structure was determined to be $[ONNO]\{Yb(\mu\text{-}O^iPr)Cl(HMPA)\}_2$ by X-ray diffraction as shown in Scheme 2. Attempts to substitute the residual chlorine atoms by other organic groups were unsuccessful. A total of 2 equiv of NaO^iPr was added to the THF solution of complex **3**, and no reaction was detected. Furthermore, complex **2** reacted even with 4 equiv of NaO^iPr in THF, and in a few days, after workup, the isolated product was identified still to be complex **3**. These results indicated that the terminal Yb−Cl bonds in complex **3** were almost inert for substituted reactions. This might be attributed to the ytterbium atoms in complex **3** being blocked by the bulky bis(phenolate) ligands and HMPA molecules, which hindered the interaction of NaO^iPr with the metal atoms.

Since the terminal chlorine atoms are inert for the substituted reaction, we wonder whether the terminal chlorine

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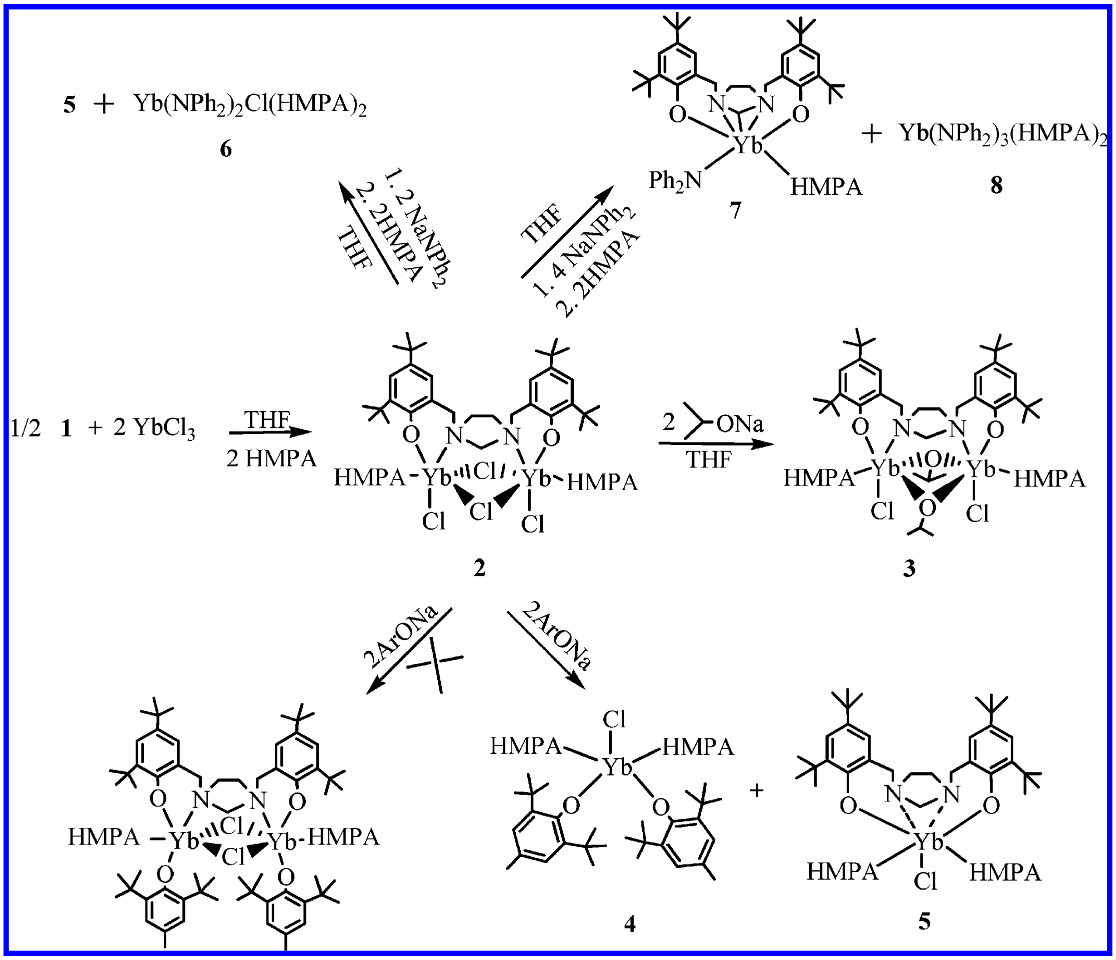
Scheme 2



atoms in complex **2** can be substituted first and the bridged ones be retained. Maybe the bridged chlorine atoms are more active and the further chloride substituted reaction can proceed smoothly. Thus, a bulky aryloxo group, 2,6-di-*tert*-butyl-4-methylphenoxo (ArO), was chosen because this ligand was usually coordinated to the lanthanide atom as a terminal group.[17] However, it was found that an unexpected ligand redistribution reaction occurred, and the dinuclear backbone was broken. Complex **2** reacted with ArONa in a 1:2 molar ratio in THF, after workup, to give two mononuclear complexes $(ArO)_2YbCl(HMPA)_2$ (**4**) and [ONNO]-$YbCl(HMPA)_2$ (**5**) in moderate isolated yields as shown in Scheme 2, which were separated according to the difference in solubility. Complex **4** was well characterized by elemental analysis and IR, and its definitive structure was determined by X-ray diffraction. The composition of complex **5** was confirmed by elemental analysis. Due to its paramagnetism, no resolvable NMR spectrum was obtained. Attempts to obtain the definitive structure failed, due to solvent loss and the deterioration in crystal quality. The occurrence of the ligand redistribution reaction might be attributed to the bulkiness of the aryloxo group. The coordination of the bulky aryloxo group to the ytterbium atom brings about the steric overcongestion around the metal atom, which induces the redistribution reaction in this system.

In order to further elucidate the effect of the bulkiness of the reagent on the outcome of the reaction, the reaction of complex **2** with another bulky reagent, sodium diphenyl amide, was explored. Complex **2** reacted with sodium diphenyl amide in a 1:2 molar ratio in THF, after workup, and the expected two ligand redistributed products **5** and **6** were isolated as microcrystals as shown in Scheme 2. The elemental analysis results of complexes **5** and **6** were consistent with the formulas of "[ONNO]$YbCl(HMPA)_2$" and "$(Ph_2N)_2YbCl(HMPA)_2$". Attempts to obtain high-quality crystals to determine their definitive structures were unsuccessful. Due to the presence of Yb−Cl bonds in complexes **5** and **6**, the complexes (ONNO)$Yb(NPh_2)$-(HMPA) (**7**) and $Yb(NPh_2)_3(HMPA)_2$ (**8**) should be isolated as the final products by the reaction of complex **2** with 4 equiv of $NaNPh_2$, if these Yb−Cl bonds are active for substitution reaction. Indeed, the expected complexes **7** and **8**, after workup, were obtained in good isolated yields from the reaction mentioned above as shown in Scheme 2. Complexes **7** and **8** were well characterized by elemental analyses and X-ray diffraction structure determination.

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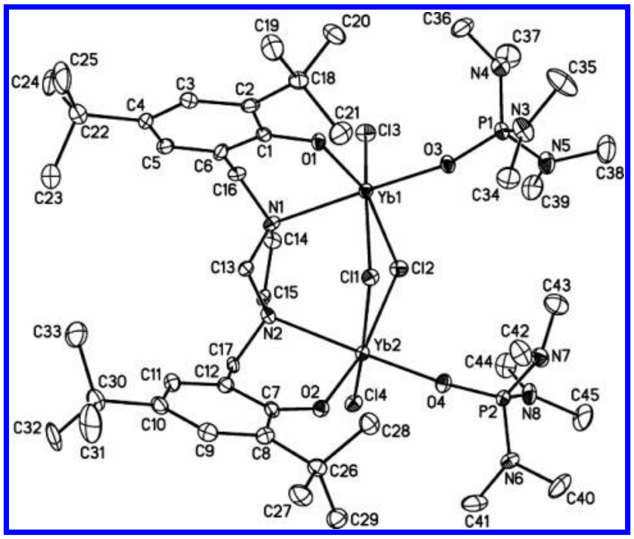

Figure 2. ORTEP diagram of complex **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

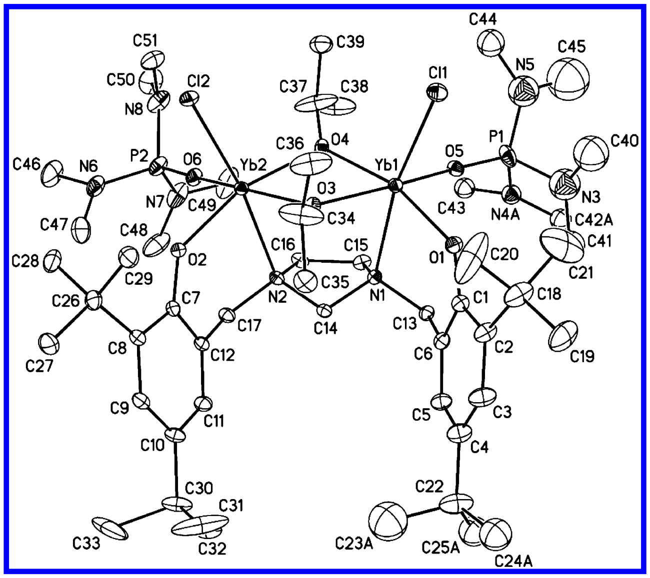

Figure 3. ORTEP diagram of complex **3** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

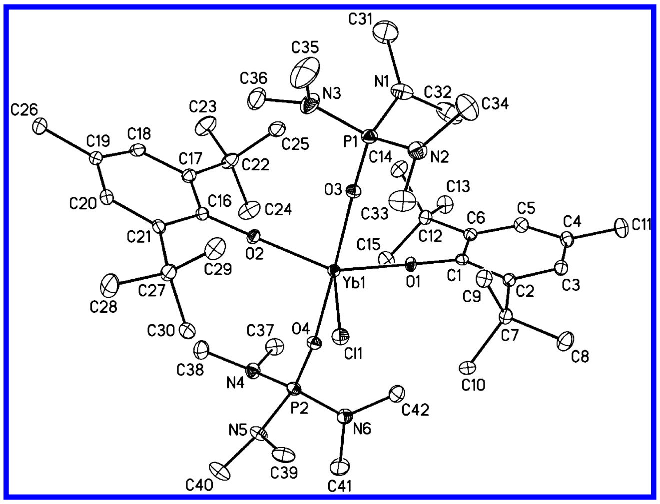

Figure 4. ORTEP diagram of complex **4** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

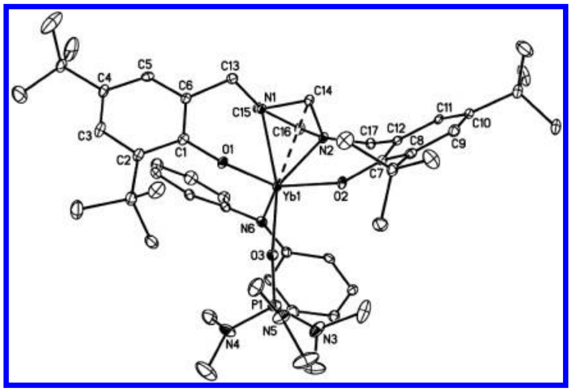

Figure 5. ORTEP diagram of complex **7** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Crystal Structures of Ytterbium Complexes. The molecular structures of complexes **2**−**4**, **7**, and **8** are shown in Figures 2−6, and selected bond lengths are given in Tables 3 and 4. Complex **2** has a dinuclear structure in which two YbCl fragments are linked by two chlorine atoms and one bridging [ONNO] ligand. Each ytterbium atom is six-coordinated by one oxygen atom and one nitrogen atom from the [ONNO] ligand, three chlorine atoms, and one oxygen atom from the HMPA molecule to form a distorted-octahedral geometry. Rare examples reported so far have the dinuclear structure linked by one multidentate ligand.[18] The coordination mode of chlorine atoms to ytterbium atom in complex **2** is the same as that in $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$.[19] The overall molecular structure of complex **3** is similar to that of complex **2**, except that two isopropoxy groups are the bridges instead of the two bridging chlorine atoms and are coordinated to the two ytterbium atoms.

In complex **2**, the Yb−O(Ar) bond lengths are 2.046(6) and 2.078(7) Å, giving an average of 2.062(6) Å, which is slightly shorter than that in $(ArO)YbCl_2(THF)_3$.[20] The averaged bridged Yb−Cl bond length of 2.688(3) Å is comparable with that observed in $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$ (2.660(3) Å)[19] and $\{[(DIPPh)_2nacnac]YbCl(\mu\text{-}Cl)_3Yb[(DIPPh)_2nacnac](THF)\}$ (2.708(2) Å) ($(DIPPh)_2nacnac$ = *N*,*N*-diisopropylphenyl-2,4-pentanediimine anion)[21] but is apparently longer than those in $[(C_5Me_5)Yb(Ph_2nacnac)(\mu\text{-}Cl)]_2$ ($Ph_2nacnac$ = *N*,*N*-diphenyl-2,4-pentanediimine anion) (2.571(3) Å).[22] The averaged terminal Yb−Cl bond length of 2.530(3) Å is comparable with those observed in $(Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O{-}C_6H_2{-}{}^tBu_2\text{-}3,5)\}_2)YbCl(THF)$ (2.5363(10) Å)[1e] and $(ArO)YbCl_2(THF)_3$ (2.555(2) Å)[20] but is slightly longer than that in $(ArO)_2YbCl(THF)_2$ (2.477(9) Å).[23] In

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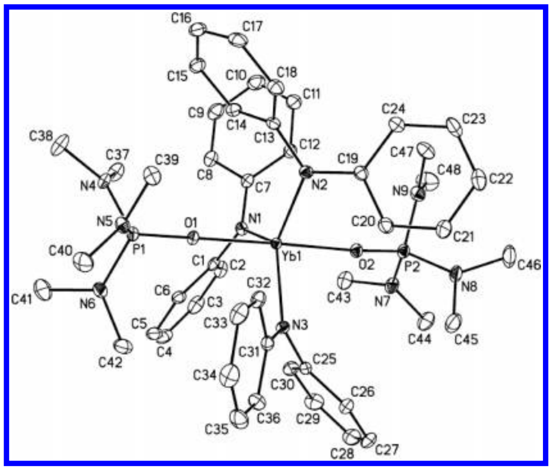

Figure 6. ORTEP diagram of complex **8** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) in Complexes **2** and **3**

	2	3		2	3
Yb(1)−O(1)	2.046(6)	2.117(5)	Yb(2)−O(2)	2.078(7)	2.121(5)
Yb(1)−O(3)	2.159(6)	2.201(5)	Yb(2)−O(4)	2.138(7)	2.272(5)
Yb(1)−O(5)		2.240(5)	Yb(2)−O(6)		2.235(5)
Yb(1)−O(4)		2.275(5)	Yb(2)−O(3)		2.203(5)
Yb(1)−Cl(3)	2.531(3)		Yb(2)−Cl(4)	2.528(3)	
Yb(1)−N(1)	2.548(8)	2.532(6)	Yb(2)−N(2)	2.543(8)	2.528(6)
Yb(1)−Cl(1)	2.665(2)	2.560(2)	Yb(2)−Cl(2)	2.684(3)	2.561(2)
Yb(1)−Cl(2)	2.701(3)		Yb(2)−Cl(1)	2.700(2)	
Yb(2)−C(17)	3.207(9)		Yb(2)−C(7)	3.179(10)	
Yb(2)−C(34)		3.137(13)	Yb(2)−C(37)		3.149(15)

addition, remote π interactions of C(17) and C(7) with Yb(2) were observed in complex **2**. The bond lengths of Yb(2)−C(17) and Yb(2)−C(7) are 3.207(9) and 3.179(10) Å, respectively, which are comparable to those of 2.986(6) and 3.180(9) Å for bridging η^2-C_5H_5 bonding in $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$,[24] and 2.814(4)−3.148(6) Å for chelating η^6-,η^1-Ph−Yb bonding in $[Yb(Odpp)_3]_2$ (Odpp = 2,6-diphenylphenolate).[25]

In complex **3**, two isopropoxy groups are unsymmetrically coordinated to two ytterbium atoms with the deviation of 0.07 Å. The averaged Yb−O(^{i}Pr) bond length is 2.238(6) Å, which is consistent with that in $[(MBMP)Yb(\mu\text{-}O^iPr)(THF)_2]$.[2b] The averaged Yb−N bond length compares well with the terminal ones in complex **2**. The averaged Yb−O(Ar) and Yb−O(HMPA) bond lengths of 2.119(5) and 2.237(5) Å, respectively, are larger than the corresponding values in complex **2** (2.062(6) and 2.148(7) Å); meanwhile, the averaged Yb−Cl bond length of 2.560(2) Å is apparently smaller than that in complex **2** (2.674(3) Å). These bond parameters indicated that the chlorine atoms in complex **3** might be shielded by bulky aryloxides and HMPA molecules, which caused the inert to substituted reaction.

Table 4. Selected Bond Lengths (Å) in Complexes **4**, **7**, and **8**

	4	7a	7b	8
Yb(1)−O(1)	2.110(3)	2.153(4)	2.144(4)	2.198(19)
Yb(1)−O(2)	2.110(3)	2.102(4)	2.094(4)	2.212(2)
Yb(1)−O(3)	2.214(3)	2.220(4)	2.219(4)	
Yb(1)−O(4)	2.217(3)			
Yb(1)−Cl(1)	2.541(10)			
Yb(1)−N(1)		2.504(4)	2.497(5)	2.305(2)
Yb(1)−N(2)		2.497(5)	2.570(5)	2.268(2)
Yb(1)−N(3)				2.288(2)
Yb(1)−N(6)		2.298(5)	2.310(5)	
Yb(1)−C(14)		2.825(6)	3.201(6)	
Yb(1)−C(40)		3.138(5)	2.871(6)	

Complexes **4**, **7**, and **8** have monomeric structure. The coordination geometries around the ytterbium atoms in complexes **4** and **8** are similar, and each ytterbium atom is five-coordinate to form a distorted trigonal bipyramid geometry. Complex **7** crystallizes with two crystallographically independent but chemically similar molecules (**7a**, **7b**) in the unit cell. Like those found in other amine or N-heterocycle bridged bis(phenolate) metal complexes,[26] two nitrogen atoms from the imidazolidine ring were found to bind to the metal center in the solid state. In addition, one carbon atom (C(14)) of the imidazolidine ring is also coordinated to the ytterbium atom. Thus, the imidazolidine ring is η^3-coordinated to the ytterbium atom, and the ytterbium atom is seven-coordinated by two oxygen atoms, two nitrogen atoms and one carbon atom from the bis(phenolate) ligands, one nitrogen atom from the amido group, and one oxygen atom from the HMPA molecule. The coordination geometry at the central metal can be best described as a distorted trigonal bipyramid if the η^3-coordinated imidazolidine ring is considered to occupy one coordination site, in which O(1), O(2), and N(6) are considered to occupy the equatorial plane.

In complex **4**, The Yb−O(Ar) bond length of 2.110(3) Å compares well with the corresponding value in $(ArO)_2YbCl(THF)_2$ (2.080(1) Å),[23] but the Yb−O(HMPA) bond lengths are relatively larger than the Yb−O(THF) bond lengths, while the Yb−Cl bond length in complex **4** is relatively smaller.

In complex **7**, the averaged Yb−O(Ar) and Yb−N(ring) bond lengths of 2.127(4) and 2.500(5) Å, respectively, are comparable with the corresponding values observed in complexes **2** and **3** and other amine bridged bis(phenolate) lanthanide complexes.[1] The Ln−N(Ph) bond length of 2.298(5) Å lies within the range of the corresponding bond lengths that have been reported for $(CH_3C_5H_4)_2YbNPh_2(THF)$, $(C_5Me_5)_2YbNPh_2$,[27] $[(DIPPh)_2nacnac]Yb(NPh_2)Cl(THF)$,[28] and $[Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}{}^tBu_2\text{-}3,5)\}_2]Yb(NPh_2)(THF)$[1e] when the effect of coordination number on the effective ionic radius is considered. It is worth noting that there is a strong π interaction of one carbon atom of the imidazolidine ring with the ytterbium atom. The Yb−C(14) bond length of 2.825(6) Å is apparently lower than the Ln−C

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contacts observed in complex **2** and the other known examples of Ln−C agostic interactions mentioned above. The Yb−C(14) bond length compares well with that observed in the neutral arene ytterbium complex Yb(η^6-HMB)$(AlCl_4)_3$ (HMB = hexamethylbenzene) (2.865(39) Å), in which the Yb−C π interaction was considered to exist unambiguously.[29] Additionally, there is a remote π interaction between the α carbon atom of the diphenylamido group with the central metal atom. The Yb−C(40) bond length of 3.138(5) Å is in accordance with the values in $[Yb(Odpp)_3]_2$ (from 2.814(4) to 3.148(6) Å). Variations in the Ln−N(Ph)−C angles are associated with the existence of π interactions in this complex. The angle that is associated with the nearby carbon atom (Yb(1)−N(6)−C(40)) is 113.8(4)°, and the other angle (Yb(1)−N(6)−C(46)) is 127.3(4)°.

In complex **8**, the Yb−N bond lengths range from 2.268(2) to 2.305(2) Å, giving an average of 2.287(2) Å, which is apparently larger than that in $Yb(NPh_2)_3(THF)_2$ (2.219(6) Å)[30] and accords well with the Yb−N bond lengths in complexes $[Yb(NPh_2)_4][Li(THF)_4]$ (2.212(9) Å)[31] and $Yb[N(SiMe_3)_2]_3$ (2.158(13) Å)[32] when the effect of coordination number on the effective ionic radius is considered.[33] It is reasonable to ascribe the difference in bond parameters to the increased steric congestion in complexes **8** and $Yb(NPh_2)_3(THF)_2$ that results from the replacement of the THF molecules by two bulky HMPA molecules.

Conclusion

A new imidazolidine-bridged bis(phenol) was prepared by a simple Mannich reaction. This compound can be used as an ancillary ligand for a series of sodium and ytterbium complexes. The bis(phenol) reacted with NaH to give sodium bis(phenolate) as a dimeric tetranuclear complex, which reacted with anhydrous $YbCl_3$ to produce a novel bimetallic ytterbium dichloride. It was found that this ytterbium dichloride can be used as a useful precursor to prepare a series of ytterbium derivatives by direct salt metathesis reactions, and the bulkiness of the reagents has profound effect on the outcome of these reactions. For the less bulky reagent, such as sodium isopropoxide, the bimetallic backbone remained, whereas for the more bulky reagents, such as sodium aryloxide and sodium diphenyl amide, the ligand redistribution reaction occurred, and the mononuclear complexes were isolated. Further studies on the synthesis and reactivity of lanthanide derivatives supported by the heteroatom-bridged bis(phenolate) ligands are in progress in our laboratory.

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Supporting Information Available: Crystallographic data for complexes **1**−**4**, **7**, and **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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