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# Synthesis, Reactivity, and Characterization of Sodium and Rare-Earth Metal Complexes Bearing a Dianionic *N*-Aryloxo-Functionalized *β*-Ketoiminate Ligand

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The synthesis and reactivity of a series of sodium and rare-earth metal complexes stabilized by a dianionic *N*-aryloxo-functionalized *β*-ketoiminate ligand were presented. The reaction of acetylacetone with 1 equiv of 2-amino-4-methylphenol in absolute ethanol gave the compound 4-(2-hydroxy-5-methylphenyl)imino-2-pentanone ($LH_2$, **1**) in high yield. Compound **1** reacted with excess NaH to afford the novel sodium cluster $[LNa_2(THF)_2]_4$ (**2**) in good isolated yield. Structure determination revealed that complex **2** has the 22-vertex cage structure. Reactions of complex **2** with anhydrous $LnCl_3$ in a 1:4 molar ratio, after workup, gave the desired lanthanide chlorides $[LLnCl(DME)]_2$ [Ln = Y (**3**), Yb (**4**), Tb (**5**)] as dimers. A further study revealed that complexes **3**−**5** are inert for chlorine substitution reactions. $(ArO)_3Ln(THF)$ (ArO = 2,6-$Bu^t_2$-4-$MeC_6H_2O$) reacted with compound **1** in a 1:1 molar ratio in tetrahydrofuran (THF), after workup, to give the desired rare-earth metal aryloxides as dimers $[LLn(OAr)(THF)]_2$ [Ln = Nd (**6**), Sm (**7**), Yb (**8**), Y (**9**)] in high isolated yields. All of these complexes are well characterized, and the definitive molecular structures of complexes **2** and **4**−**6** were determined. It was found that complexes **6**−**9** can be used as efficient initiators for L-lactide polymerization, and the ionic radii of the central metals have a significant effect on the catalytic activity.

## Introduction

Over the past few years, *β*-ketoiminate ligands have become among the most attractive chelating systems in main-group and transition-metal coordination chemistry because of their ease of preparation from inexpensive and readily available starting materials and sample modification of both steric and/or electronic properties. The metal complexes stabilized by these ligand systems have been used in a variety applications.[1−5] For example, they are widely used as the precursors for metal−organic chemical vapor deposition (MOCVD) for the growth of thin films.[1] Some recent papers reported that these metal complexes can also be employed in homogeneous catalysis, involving catalysts for the organic synthesis,[3] the polymerization and copolymerization of olefins,[4] and the ring-opening polymerization of cyclic esters, etc.[5] Thus, it is surprising that rare-earth metal complexes with such ligands were by far less studied than other metal complexes.[6]

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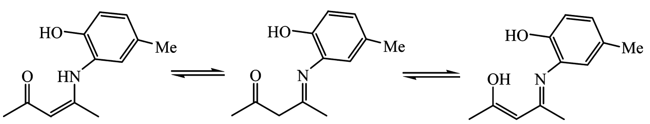
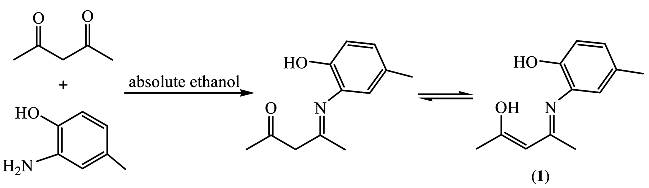
**Chart 1**



**Scheme 1**



(1)

As one of the derivatives of $\beta$-ketoiminate ligands, the *N*-aryloxo-functionalized $\beta$-ketoimines contain a pendant phenol functionality and have been known for about a century.[7] They have tautomeric forms as shown in Chart 1 and are capable of coordinating to a metal center in a tridentate (2−) or bidentate (1−) manner. They were employed in main-group and transition-metal coordination chemistry about 4 decades ago[8] but not in lanthanide chemistry. Bearing in mind the development of multidentate ligands with varying combinations of donor atoms and charges,[9] it would be interesting to introduce these ligands into organolanthanide chemistry.

In recent years, there is considerable interest in developing structurally well-characterized lanthanide complexes as homogeneous catalysts for the ring-opening polymerization of lactide because of the biodegradable and biocompatible nature of polylactides and their wide applications in medicine, pharmaceutics, and tissue engineering. Lanthanide alkoxides (aryloxides) are well-known to be highly efficient initiators for the ring-opening polymerization of lactide to give polylactide with high molecular weight and narrow molecular weight distribution.[10] The properties of polylactides depend strongly on their tacticity. Ring-opening polymerization of L-lactide, an enantiomerically pure monomer, can provide isotactic poly(L-lactide), which is a highly crystalline material. In this contribution, the sodium salt and a series of rare-earth metal complexes stabilized by an *N*-aryloxo-functionalized $\beta$-ketoiminate ligand were synthesized, and it was found that the corresponding rare-earth metal aryloxides are efficient initiators for L-lactide polymerization. Herein, we report these results.

## Results and Discussion

**Synthesis and Characterization of the Ligand and Its Sodium Salt.** The reaction of 2,4-pentanedione with 1 equiv of 2-amino-4-methylphenol in absolute ethanol, after workup, gave the *N*-aryloxo-functionalized $\beta$-ketoimine 4-(2-hydroxy-5-methylphenyl)imino-2-pentanone ($LH_2$, **1**) in high isolated yield, as shown in Scheme 1. Compound **1** was identified by elemental analysis and IR spectroscopy. $^1H$

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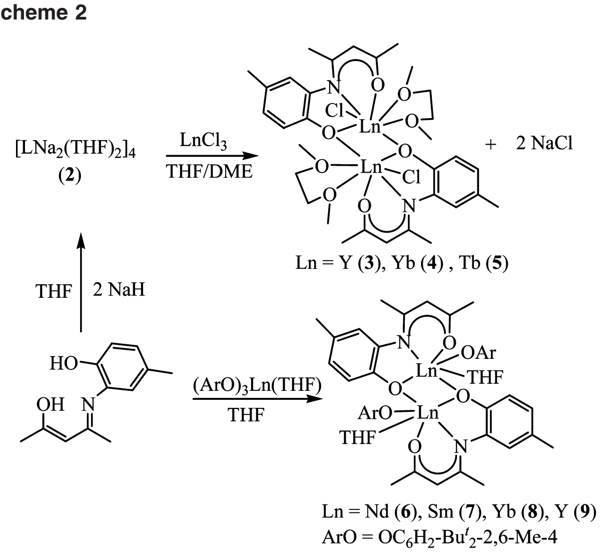
**Scheme 2**



NMR spectroscopy revealed that compound **1** exists as an imine-enol mode in solution.

Generally, the sodium derivatives of the ligands can be used as the starting materials for the synthesis of the transition-metal complexes via transmetalation reactions. It has been reported that the sodium aryloxides or alkoxides have generally polynuclear solid-state structures with differences on the steric bulk and electron effect.[11] Thus, the sodium salt of the ligand $LH_2$ was prepared. Compound **1** reacted with NaH in tetrahydrofuran (THF) at room temperature, after workup, to afford the corresponding disodium salt as tetramer $[LNa_2(THF)_2]_4$ (**2**) as orange-yellow microcrystals in 68% yield, as shown in Scheme 2. The composition of complex **2** was confirmed by elemental analysis and $^1H$ NMR spectroscopy, and its definitive molecular structure was determined by single-crystal structure analysis. To our best knowledge, there are few examples of a structurally characterized metal complex supported by an *N*-aryloxo-functionalized $\beta$-ketoiminate ligand.[12] Complex **2** is sensitive to air and moisture, and it is soluble in THF, slightly soluble in toluene, and insoluble in hexane.

The molecular structure of complex **2** determined by X-ray diffraction analysis is provided in Figure 1, and the core structure is shown in Figure 2, with its selected bond lengths. Complex **2** is an octanuclear tetramer. The core structure is a 22-vertex cage, which is made up from eight sodium cations, eight oxygen atoms, and four nitrogen atoms from four $\beta$-ketoiminate ligands as well as two oxygen atoms from two THF molecules, as shown in Figure 2. The eight sodium atoms form two slightly distorted triangular prisms, in which the plane defined by Na1, Na2, Na3, and Na4 is shared. The coordination environments around the sodium atoms can be divided into two kinds. Two sodium atoms (Na2 and Na4) are five-coordinated with five oxygen atoms to form the distorted trigonal-bipyramidal geometries, whereas the other sodium atoms are six-coordinated to form distorted octahedral geometries. It is worth noting that there are four coordination modes for the oxygen atoms in one molecule. The aryloxo and alkoxo oxygen atoms adopt $\mu_4$- and $\mu_3$-bridging coordination modes, respectively; the two oxygen

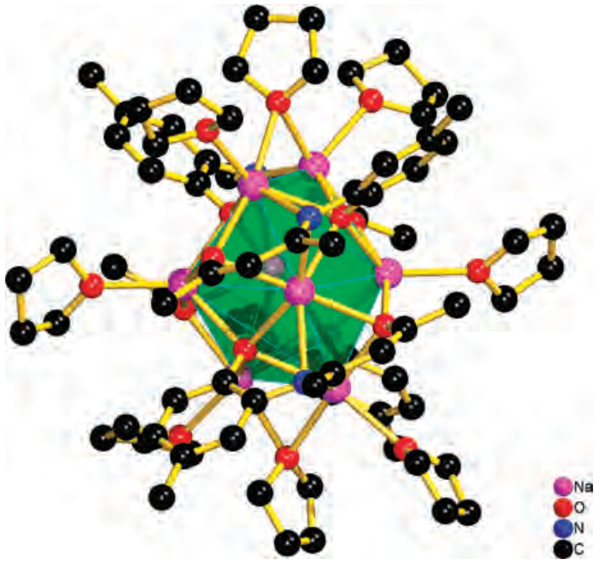


**Figure 1.** Molecular structure of complex **2**. Hydrogen atoms are omitted for clarity.

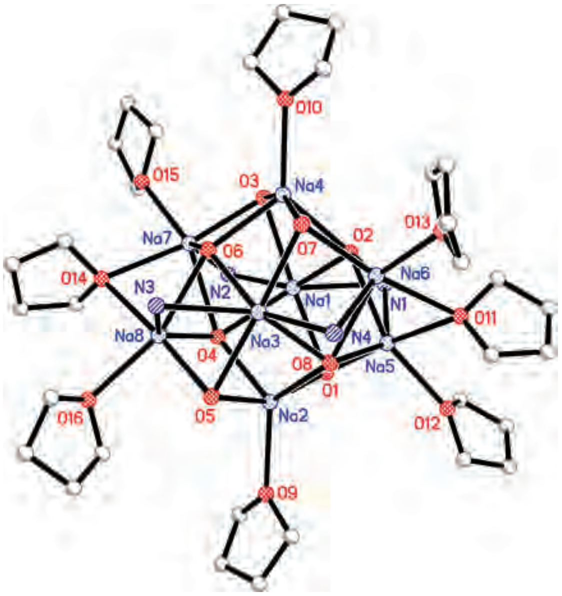


**Figure 2.** Core structure of complex **2**. Selected bond lengths (Å): Na1−O1 2.454(2), Na1−O2 2.378(2), Na1−O3 2.526(2), Na1−O4 2.406(2), Na1−N1 2.563(2), Na1−N2 2.543(2), Na2−O1 2.348(2), Na2−O4 2.413(2), Na2−O5 2.366(2), Na2−O8 2.384(2), Na2−O9 2.451(2), Na3−O5 2.479(2), Na3−O6 2.376(2), Na3−O7 2.503(2), Na3−O8 2.359(2), Na3−N3 2.571(2), Na3−N4 2.531(2), Na4−O2 2.367(2), Na4−O3 2.365(2), Na4−O6 2.360(2), Na4−O7 2.368(2), Na4−O10 2.428(2), Na5−O1 2.303(2), Na5−O2 2.581(2), Na5−O8 2.322(2), Na5−O11 2.511(2), Na5−O12 2.444(2), Na5−N1 2.445(2), Na6−O2 2.305(2), Na6−O7 2.339(2), Na6−O8 2.622(2), Na6−O11 2.557(2), Na6−O13 2.402(2), Na6−N4 2.411(2), Na7−O3 2.330(2), Na7−O4 2.588(2), Na7−O6 2.314(2), Na7−O14 2.528(2), Na7−O15 2.416(2), Na7−N2 2.409(2), Na8−O4 2.322(2), Na8−O5 2.309(2), Na8−O6 2.542(2), Na8−O14 2.473(2), Na8−O16 2.433(2), Na8−N3 2.421(2).

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atoms from two THF molecules (O11 and O14) adopt a $\mu$-bridging coordination mode, and the six oxygen atoms from the other THF molecules are terminal. The Na−O(aryloxo) bond lengths range from 2.305(2) to 2.622(2) Å, giving an average of 2.415(2) Å, which is comparable with the averaged Na−O($\mu_4$-aryloxo) bond length in $[NaOC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4]_4$ [2.421(7) Å][11a] and $[NaOC_6H_4(CH_2NMe_2)_2\text{-}2]_6$ (2.434 Å)[11b] but is slightly larger than those found in other sodium aryloxo complexes $[(4\text{-}F\text{-}C_6H_4ONa)_6(dioxane)_3]_\infty$ (2.340 Å),[13] $[(4\text{-}F\text{-}C_6H_4ONa)_6(THF)_8]$ (2.356 Å),[13] and $\{[ONNO]Na_2(THF)_2\}_2$ (2.217 Å) [ONNO = 1,4-bis(2-*O*-3,5-di-*tert*-butylbenzyl)imidazolidine].[9g] The averaged Na−O(alkoxo) bond length of 2.391(1) Å is apparently larger than the Na−O($\mu_3$-alkoxo) bond lengths in $LnNa_8(OCMe_3)_{10}Cl$ [Ln = Eu, 2.305(9) Å; Y, 2.284(5) Å][14] and $[Na_{11}(OCMe_3)_{10}(OH)]$ [2.250(9) Å].[15]

**Synthesis and Characterization of the Rare-Earth Metal Complexes.** It was found that the sodium salt of *N*-aryloxo-functionalized $\beta$-ketoiminate can be used as the starting material for the synthesis of neutral rare-earth metal complexes via a general metathesis reaction. Reactions of anhydrous $LnCl_3$ with complex **2** (or formed in situ) in a 4:1 molar ratio in THF, after workup, gave the final products $[LLnCl(DME)]_2$ [Ln = Y (**3**), Yb (**4**), Tb (**5**)] in yields of up to 75% (Scheme 2). Elemental analysis results revealed that the complexes consist of one dianionic ligand L, one chlorine atom, and one coordinated 1,2-dimethoxyethane (DME) molecule at the metal center. Further X-ray molecular structure determination of complexes **4** and **5** confirmed that they have solvated dimeric structures. The $^1H$ NMR spectrum of complex **3** in $C_6D_6$ revealed a loss of symmetry of the *N*-aryloxo $\beta$-ketoiminate ligands such that two methyl hydrogen signals on the arene rings were observed, which indicated that the dimeric structure was kept in solution. The crystals of complexes **4** and **5** are relatively stable to air and moisture and can be exposed to air for a few hours without apparent deterioration, but the color of the solution changes immediately when the solution is exposed to air. Complexes **3**−**5** are soluble in THF and slightly soluble in DME and toluene.

Complexes **4** and **5** are isostructural, and both complexes crystallize with three crystallographically independent but chemically similar molecules (**4a**−**c** and **5a**−**c**) and two molecules of cocrystallized THF in the unit cell. The main differences among these molecules are that they have different bond parameters. The molecular structure diagram of complex **4a** is shown in Figure 3, with the selected bond lengths of complexes **4a** and **5a** (in brackets). Complexes **4** and **5** possess bridging phenoxo oxygen atoms rather than dimerize via the chloride ligands, which might be attributed to the lack of a substituted group on the ortho position of the arene ring. A similar coordination mode has been reported in amine-bridged bis(phenolate)scandium chloride.[16] The molecules have $C_2$ symmetry, and each lanthanide atom is seven-coordinated with two oxygen atoms and one nitrogen atom from one $\beta$-ketoiminate ligand, two oxygen atoms from one DME molecule, one chlorine atom, and one oxygen atom from another $\beta$-ketoiminate ligand. The lanthanide centers have distorted capped trigonal-prismatic geometries, with the capping atoms being the chlorine atoms. The Ln−O(alkoxo) and Ln−N bond lengths of 2.140(4) [2.188(4)] and 2.399(4) [2.452(4)] Å (with data for **5a** in brackets), respectively, are in accordance with the corresponding bond lengths in ytterbium $\beta$-ketoiminate complex $Yb[OC(Bu^t)CHC(Bu^t)NPr]_3$ (2.15 and 2.42 Å),[6g] revealing a similar $\pi$-electron delocalization present within the *N*-aryloxo $\beta$-ketoiminate ligands in these complexes. As expected, the bridging Ln−O(Ar) bond length of 2.260(3) [2.319(3)] Å is larger than the value of the terminal bond in $(ArO)_2YbCl(THF)_2$ ($ArO = OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4$) [2.080(1) Å],[17] even when the effect of the coordination number on the effective ionic radius is considered.

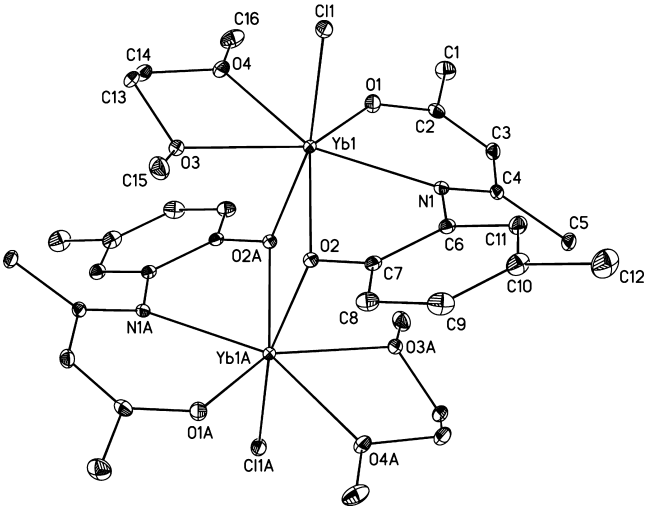

**Figure 3.** ORTEP diagram of complex **4** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 10% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (with data for **5a** in brackets): Ln1−O1 2.140(4) [2.188(4)], Ln1−O2 2.269(3) [2.326(3)], Ln1−O2A 2.251(3) [2.312(3)], Ln1−O3 2.434(3) [2.484(3)], Ln1−O4 2.455(3) [2.507(4)], Ln1−N1 2.399(4) [2.452(4)], Ln1−Cl1 2.552(2) [2.612(2)]; O2−Ln1−O2A 71.3(1) [70.9(1)], O2A−Ln1−O4 86.4(1) [85.6(1)], N1−Ln1−O2 68.6(1) [67.8(1)], O4−Ln1−N1 151.0(1) [151.2(1)], O2A−Ln1−Cl1 165.89(9) [164.72(9)].

A further study revealed that complexes **3**−**5** cannot be used as precursors for the synthesis of the expected rare-earth metal derivatives. Chloride substitution reactions of complexes **3**−**5** with a range of lithium alkyls or sodium amides and aryloxides were unsuccessful, and the isolated complexes are the starting materials.

Well-defined rare-earth metal aryloxides supported by the *N*-aryloxo-functionalized $\beta$-ketoiminate ligand can be conveniently prepared through protonolysis reactions of $(ArO)_3Ln(THF)$ with 1 equiv of $LH_2$ in THF, as summarized

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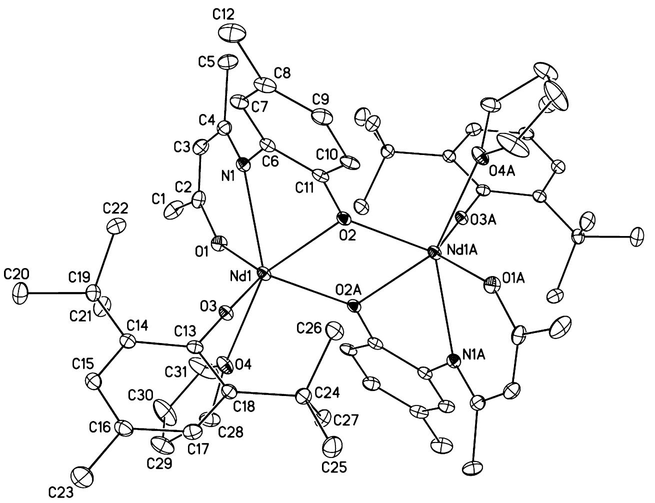

**Figure 4.** ORTEP diagram of complex **6** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 10% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd1−O1 2.260(5), Nd1−O2 2.409(4), Nd1−O2A 2.334(5), Nd1−O3 2.177(4), Nd1−O4 2.548(5), Nd1−N1 2.529(6); O2−Nd1−O2A 68.8(2), O2A−Nd1−O4 85.8(2), N1−Nd1−O2 65.7(2), O4−Ln1−N1 143.1(2), O1−Nd1−O3 129.5(9).

in Scheme 2. When a THF solution of $(ArO)_3Ln(THF)$ was added to a THF solution of $LH_2$ in a 1:1 molar ratio at room temperature, the color of the solution changed immediately from purple-blue to blue (for Nd), red to orange-yellow (for Yb), and colorless to yellow (for Y). After workup, blue [Nd (**6**)], yellow [Sm (**7**) and Yb (**8**)], and pale-yellow [Y (**9**)] crystals were obtained from a concentrated THF solution at −10 °C in 62−76% isolated yields. The compositions of complexes **6**−**9** were established as LLn(OAr)(THF) by elemental analysis and $^1$H NMR spectroscopy in the case of complex **9**. Definitive molecular structure determination of complex **6** revealed that this complex has a dimeric structure $[LNd(OAr)(THF)]_2$ in the solid state. Attempts to determine the definitive molecular structures of complexes **7**−**9** were unsuccessful because of solvent loss and deterioration in the crystal quality. We proposed that complexes **7**−**9** exist as dimers in the solid state according to the structure of the analogous complex **6**. All of these complexes are moderately sensitive to air and moisture. They are soluble in THF and toluene, and their solubility in toluene increases with a decrease in the ionic radius of the central metal.

The X-ray molecular structure of complex **6** is shown in Figure 4 with its selected bond lengths and angles. Complex **6** has a centrosymmetric dimeric structure containing a $Nd_2O_2$ core bridging through the phenoxo oxygen atoms from two $\beta$-ketoiminate ligands, which is similar to those observed in complexes **4** and **5**. The metal centers in this complex are six-coordinated with two oxygen atoms and one nitrogen atom from one $\beta$-ketoiminate ligand, one oxygen atom from a aryloxo group, one oxygen atom from one THF molecule, and one oxygen atom from another $\beta$-ketoiminate ligand. Each metal center has a highly distorted octahedral coordination geometry, in which O2, O2A, O4, and N1 can be considered to occupy equatorial positions and O1 and O3 occupy axial positions.

In complex **6**, the terminal Nd−O(Ar) bond length of 2.177(4) Å is apparently smaller than the corresponding values in $[(ArO)_3Nd(THF)]$ [2.176(3) Å],[18] $[Na(THF)_6][Nd(ArO)_4]$ [2.230(5) Å],[18] $K[Nd(OC_6H_3Pr^i{}_2\text{-}2,6)]$ (2.211 Å),[19] and $Nd(Odpp)_3$ (Odpp = $C_6H_3Ph_2$-2.6) (2.169(4) Å),[20] when the effect of the coordination number on the effective ionic radius is considered. The terminal Nd−O(alkoxo) bond length of 2.260(5) Å is comparable with the corresponding bond length in complexes **4** and **5**, when the difference in the ionic radii is considered. However, this bond length is apparently smaller than the bridged Nd−O(alkoxo) bond lengths in bridged bis(phenolate)neodymium alkoxo complexes [ave 2.360(5) and 2.368(6) Å].[9g,h] These differences in the bond parameters reflected the less steric congestion around central metal atoms due to the less bulkiness of the $\beta$-ketoiminate ligand. Two phenoxo groups are unsymmetrically coordinated to the central metal atoms with a deviation of 0.075 Å. As expected, the bridged Nd−O(Ar) bond lengths of 2.409(4) and 2.334(5) Å are larger than the terminal ones.

**Polymerization of L-Lactide Initiated by Complexes 6−9.** The catalytic activity of the new $\beta$-ketoiminate rare-earth metal aryloxo complexes toward the ring-opening polymerization of L-lactide was explored, and the results are summarized in Table 1.

It can be seen that all of the rare-earth metal aryloxo complexes can initiate the polymerization of L-lactide in toluene. Complex **6** gives 30% yield of 200 equiv of L-lactide after 1 h, and the yield reaches 85% after 2 h (entries 1 and 2). As expected, the polymerization at higher temperature was faster than that at lower temperature (entries 3 and 6). The central metal ion has a significant effect on the catalytic activity. The neodymium and samarium aryloxo complexes are efficient initiators for this polymerization: almost complete yields were achieved in toluene in 4 h at 70 °C when the molar ratio of monomer to initiator ($[M_0]/[I_0]$) is 400 (entries 7 and 11). Upon a decrease of the ionic radii, the catalytic activity decreased dramatically. The yield is 35% under the same polymerization conditions using an yttrium complex (**9**) as the initiator (entry 16), whereas the yield is only 40% even when the molar ratio of monomer to initiator decreased to 100 when the ytterbium complex (**8**) was used as the initiator (entry 13). A similar active trend is also observed when the bis(allyl) diketiminatolanthanide complexes were used as the initiators for lactide polymerization.[21] In comparison with the industrially used catalyst $Sn(Oct)_2$, these rare-earth metal aryloxides displayed relatively high activity, and the activity is comparable with those of most aluminum and zinc metal complexes reported in the literature.[10] However, complexes **6**−**9** are less active than the bis(allyl) diketiminatolanthanide complexes and amidinato-

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**Table 1.** Polymerization of L-Lactide Initiated by Complexes **6−9**[a]

| entry | initiator | $[M]_0/[I]_0$[b] | $T$ (°C) | $t$ (h) | yield (%)[c] | $M_{n,cald}$ ($10^{-4}$)[d] | $M_{n,exp}$ ($10^{-4}$)[e] | PDI |
|---|---|---|---|---|---|---|---|---|
| 1 | **6** | 200:1 | 60 | 1 | 30 | 0.86 | 3.42 | 1.56 |
| 2 | **6** | 200:1 | 60 | 2 | 85 | 2.45 | 4.19 | 1.77 |
| 3 | **6** | 400:1 | 60 | 2 | 52 | 3.00 | 3.31 | 1.78 |
| 4 | **6** | 400:1 | 70 | 15 min | trace | | | |
| 5 | **6** | 400:1 | 70 | 0.5 | 23 | | | |
| 6 | **6** | 400:1 | 70 | 2 | 75 | 4.32 | 6.21 | 1.74 |
| 7 | **6** | 400:1 | 70 | 4 | 96 | 5.53 | 8.47 | 1.73 |
| 8 | **6** | 500:1 | 70 | 4 | 50 | 3.60 | 5.17 | 1.74 |
| 9 | **7** | 200:1 | 70 | 4 | 95 | 2.74 | 7.77 | 1.62 |
| 10 | **7** | 300:1 | 70 | 4 | 96 | 4.15 | 11.8 | 1.52 |
| 11 | **7** | 400:1 | 70 | 4 | 97 | 5.94 | 13.1 | 1.61 |
| 12 | **7** | 500:1 | 70 | 4 | 20 | 1.44 | 4.49 | 1.45 |
| 13 | **8** | 100:1 | 70 | 4 | 40 | 0.58 | 1.97 | 2.37 |
| 14 | **8** | 200:1 | 70 | 4 | 20 | | | |
| 15 | **9** | 300:1 | 70 | 4 | 92 | 3.98 | 14.5 | 1.44 |
| 16 | **9** | 400:1 | 70 | 4 | 35 | 2.02 | 7.08 | 1.35 |

[a] Polymerization conditions: toluene as the solvent, [LLA] = 1 mol $L^{-1}$. [b] $[M]_0/[I]_0$ = [monomer]/[initiator]. [c] Yield: weight of polymer obtained/weight of monomer used. [d] $M_{n,calcd} = ([LA]_0/[I]_0) \times 144.13 \times$ conv %. [e] Determined by GPC analysis in THF calibrated with standard poly(styrene) and corrected using the Mark−Houwink factor of 0.58.

ytterbium amides, with reaction times being significantly longer.[21,22]

All of the polymers obtained have high molecular weights, and the measured number-average molecular weights are quite superior to the theoretical values (calculated on the assumption that each aryloxo group initiates the polymerization). This could be attributed to the low initiator efficiency. Meanwhile, there is no linear relationship between the molecular weights and the molar ratios of monomer to initiator, and the molecular weight distributions (PDIs) of the resultant polymers were relatively broad. These results indicated that these polymerization systems are not well-controlled. A possible explanation is that these results are related to the slow initiation rate and the relatively fast propagation rate.[23] Because complexes **6−9** form stable dimeric structures via the bridging phenoxo oxygen atoms, the dimeric structure could not be cleaved by the monomer; on the other hand, there are bulky substituted groups on the ortho positions of the arene ring of the aryloxo group. Therefore, the insertion of lactide into the Ln−O(aryloxo) bond becomes difficult (the presence of a short induction period even using complex **6** as the initiator at 70 °C, entry 4).

## Conclusion

The dianionic *N*-aryloxo-functionalized $\beta$-ketoiminate ligand can be used to stabilize a series of coordination complexes of sodium and rare-earth metal. The rare-earth metal complexes can be prepared by salt metathesis or protonolysis reactions. The structural features of some of these complexes were provided. The *N*-aryloxo-functionalized $\beta$-ketoiminate ligand has an overwhelming tendency to form the dimeric species for the rare-earth metal complexes. These complexes represent the first structurally characterized examples of rare-earth metal complexes bearing an *N*-aryloxo $\beta$-ketoiminate ligand. The $\beta$-ketoiminate rare-earth metal aryloxo complexes were found to be efficient initiators for the ring-opening polymerization of L-lactide. These results indicated that the *N*-aryloxo-functionalized $\beta$-ketoiminate ligands might have great potential in the design and synthesis of rare-earth metal catalysts for homogeneous catalysis.

## Experimental Section

**General Procedures.** The complexes described below are sensitive to air and moisture. Therefore, all manipulations were performed under pure argon with rigorous exclusion of air and moisture using Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. $(ArO)_3Ln(THF)$ was prepared according to a literature procedure.[18] The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Rare-earth metal analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer.[24] 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 FT-IR spectrometer as KBr pellets. The $^1H$ NMR spectra were recorded in a $C_6D_6$ solution for the sodium and yttrium complexes and in a $CDCl_3$ solution for the ligand with a Unity Varian-400 spectrometer.

**$LH_2$ (1).** To a solution of 2,4-pentanedione (11.0 g, 0.11 mol) in absolute ethanol (60 mL) was added dropwise at room temperature 2-amino-4-methylphenol (13.5 g, 0.10 mol) in absolute ethanol (30 mL). After the reaction mixture was stirred in an oil bath and refluxed for 2 h under an argon atmosphere, the mixture was concentrated to about 25 mL under reduced pressure. Ligand $LH_2$ was obtained as white block crystals by filtration in the next day (14.9 g, 73%). Mp: 180−181 °C (dec). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.24; H, 7.32; N, 6.83. Found: C, 70.11; H, 7.41; N, 6.71. $^1H$ NMR ($CDCl_3$): 1.73 (s, 3H, $CH_3C{=}N$), 2.06 (s, 3H, $CH_3C{=}O$), 2.20 (s, 3H, $CH_3$ (arene)), 5.15 (s, H, CH), 6.82−7.26 (3H, Ar), 8.51 (s, 1H, $C{=}C{-}OH$), 11.67 (s, 1H, PhOH). IR (KBr, $cm^{-1}$): 3426 (s), 3067 (s), 2751 (s), 2596 (s), 1597 (s), 1528 (s), 1431 (s), 1377 (s), 1304 (s), 1211 (s), 1127 (s), 1026 (m), 941 (m), 814 (s), 771 (s), 709 (m), 617 (w), 467 (w).

**$[LNa_2(THF)_2]_4$ (2).** A THF (20 mL) solution of $LH_2$ (1.13 g, 5.50 mmol) was added dropwise to a NaH suspension (18 mmol) in THF (20 mL) at room temperature. The reaction mixture was

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stirred overnight, and then the mixture was filtered. The transparent orange-yellow solution was concentrated under reduced pressure. Orange-yellow crystals were obtained from THF (15 mL) by filtration and then drying under reduced pressure at room temperature after 1 week (1.12 g, 68%). Mp: 91−93 °C (dec). Anal. Calcd for $C_{80}H_{116}N_4Na_8O_{16}$: C, 64.43; H, 7.05; N, 4.70. Found: C, 64.02; H, 7.25; N, 4.56. $^1$H NMR ($C_6D_6$): 1.44 (s, 3H, $CH_3C{=}N$), 1.70 (s, 4H, THF), 1.95 (s, 3H, $CH_3C{=}O$), 2.41 (s, 3H, $CH_3$ (arene ring)), 3.58 (s, 4H, THF), 4.87 (s, H, CH), 6.67−7.21 (3H, Ar). IR (KBr, $cm^{-1}$): 2956 (s), 2915 (m), 1601 (s), 1549 (s), 1449 (s), 1348 (s), 1243 (s), 1158 (s), 1023 (w), 936 (w), 824 (m), 746 (w), 625 (m).

**$[LYCl(DME)]_2$ (3). Method A.** Complex **2** (2.03 g, 1.29 mmol) in THF (30 mL) was added to the suspension of anhydrous $YCl_3$ (1.01 g, 5.17 mmol) in THF (30 mL). The color of the solution gradually changed to pale yellow, and a colorless gel-like precipitate formed gradually. The mixture was stirred at room temperature overnight, and the precipitate was removed by centrifugation. The solvent was removed under reduced pressure, and the residue was extracted with toluene (50 mL). DME (2 mL) was added to the toluene solution, and then the solution was concentrated to about 20 mL. Pale-yellow microcrystals were obtained at room temperature in a few days (1.47 g, 68%). Mp: 195−197 °C (dec). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_8Y_2$: C, 46.01; H, 5.55; N, 3.35; Y, 21.28. Found: C, 46.47; H, 5.53; N, 3.12; Y, 21.01. $^1$H NMR ($C_6D_6$): 1.45 (s, 6H, $CH_3C{=}N$), 2.15 (s, 6H, $CH_3C{=}O$), 2.45 (s, 3H, $CH_3$ (arene ring)), 2.53 (s, 3H, $CH_3$ (arene ring)), 3.16 (s, 12H, $CH_3O$ (DME)), 3.37 (s, 8H, $CH_2O$ (DME)), 4.83 (s, 2H, CH), 7.00−7.40 (m, 6H, Ar). IR (KBr, $cm^{-1}$): 2959 (m), 1597 (s), 1539 (s), 1435 (m), 1408 (m), 1362 (m), 1250 (m), 1207 (w), 1119 (w), 933 (w), 829 (w), 818 (w).

**Method B.** A THF (30 mL) solution of $LH_2$ (1.07 g, 5.17 mmol) was added dropwise to a NaH suspension (18 mmol) in THF (20 mL) at room temperature. The reaction mixture was stirred overnight, and then the mixture was filtered. The orange-yellow solution was added to the suspension of anhydrous $YCl_3$ (1.01 g, 5.17 mmol) in THF (30 mL). The following procedure is similar to that described for method A, and complex **3** was isolated as pale-yellow microcrystals (1.34 g, 62%).

**$[LYbCl(DME)]_2$ (4).** The synthesis of complex **4** was carried out in the same way as that described for complex **3** (method B), but $YbCl_3$ (1.61 g, 5.76 mmol) was used instead of $YCl_3$. Yellow microcrystals were obtained from a THF/DME solution at room temperature (2.08 g, 72%). Mp: 186−188 °C (dec). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_8Yb_2$: C, 38.29; H, 4.62; N, 2.79; Yb, 34.48. Found: C, 38.03; H, 4.70; N, 2.54; Yb, 34.63. IR (KBr, $cm^{-1}$): 2959 (m), 2924 (m), 1597 (s), 1543 (s), 1508 (s), 1435 (m), 1408 (m), 1362 (m), 1339 (m), 1288 (m), 1254 (m), 1207 (w), 1119 (w), 1022 (w), 937 (w), 864 (w). The crystals suitable for an X-ray diffraction analysis were obtained by the slow cooling of a hot THF/DME solution.

**$[LTbCl(DME)]_2$ (5).** The synthesis of complex **5** was carried out in the same way as that described for complex **3** (method B), but $TbCl_3$ (1.61 g, 6.07 mmol) was used instead of $YCl_3$. Yellow microcrystals were obtained from a THF/DME solution at room temperature (2.22 g, 75%). Mp: 178−180 °C (dec). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_8Tb_2$: C, 39.40; H, 4.75; N, 2.87; Tb, 32.59. Found: C, 49.85; H, 4.84; N, 2.63; Tb, 32.89. IR (KBr, $cm^{-1}$): 2936 (m), 1593(s), 1535 (s), 1539 (s), 1435 (m), 1404 (m), 1381 (m), 1250 (m), 1119 (m), 1100 (m), 1022 (m), 934 (m), 860 (m), 829 (m), 760 (w). The crystals suitable for an X-ray diffraction analysis were obtained by the slow cooling of a hot THF/DME solution.

**$[LNd(OAr)(THF)]_2$ (6).** A THF solution (20 mL) of $(ArO)_3Nd(THF)$ (3.05 mmol) was added to a THF solution (20 mL) of $LH_2$ (0.63 g, 3.05 mmol). The mixture was stirred overnight at room temperature, and then the solution was concentrated under vacuum. Blue crystals were obtained from a concentrated THF solution (10 mL) at −10 °C (1.20 g, 62%). Mp: 187−189 °C (dec). Anal. Calcd for $C_{62}H_{88}N_2O_8Nd_2$: C, 58.29; H, 6.89; N, 2.19; Nd, 22.59. Found: C, 58.70; H, 6.70; N, 2.09; Nd, 22.17. IR (KBr, $cm^{-1}$): 2956 (s), 2917 (m), 2871 (m), 1598 (s), 1450 (s), 1436 (s), 1358 (s), 1273 (s), 1158 (s), 1027 (w), 934 (w), 826 (m), 764 (w), 602 (w), 502 (w).

**$[LSm(OAr)(THF)]_2$ (7).** The synthesis of complex **7** was carried out in the same way as that described for complex **6**, but $(ArO)_3Sm(THF)$ (2.50 mmol) was used instead of $Nd(OAr)_3(THF)$. Yellow crystals were isolated (1.23 g, 76%). Mp: 182−184 °C (dec). Anal. Calcd for $C_{62}H_{88}N_2O_8Sm_2$: C, 57.73; H, 6.83; N, 2.17; Sm, 23.34. Found: C, 57.32; H, 6.83; N, 2.36; Sm, 22.76. IR (KBr, $cm^{-1}$): 2957 (m), 2917 (m), 2871 (m), 1595 (s), 1493 (s), 1434 (s), 1356 (s), 1272 (s), 1158 (s), 1024 (w), 933 (w), 821 (m), 763 (m), 624 (m), 503 (s).

**$[LYb(OAr)(THF)]_2$ (8).** The synthesis of complex **8** was carried out in the same way as that described for complex **6**, but $(ArO)_3Yb(THF)$ (3.10 mmol) was used instead of $(ArO)_3Nd(THF)$. Yellow crystals were obtained from a THF solution at −10 °C (1.30 g, 63%). Mp: 178−180 °C (dec). Anal. Calcd for $C_{62}H_{88}N_2O_8Yb_2$: C, 55.77; H, 6.60; N, 2.10; Yb, 25.54. Found: C, 55.80; H, 6.97; N, 1.90; Yb, 25.14. IR (KBr, $cm^{-1}$): 2959 (s), 2917 (m), 2870 (m), 1593 (s), 1497 (s), 1431 (s), 1362 (s), 1289 (m), 1157 (w), 1026 (w), 934 (w), 837 (w), 768 (w), 621 (w), 505 (w).

**$[LY(OAr)(THF)]_2$ (9).** The synthesis of complex **9** was carried out in the same way as that described for complex **6**, but $(ArO)_3Y(THF)$ (2.20 mmol) was used instead of $(ArO)_3Nd(THF)$. Pale-yellow crystals were obtained from a concentrated THF solution at −10 °C (0.85 g, 66%). Mp: 149−151 °C (dec). Anal. Calcd for $C_{62}H_{88}N_2O_8Y_2$: C, 63.61; H, 7.55; N, 2.40; Y, 15.25. Found: C, 63.61; H, 7.69; N, 2.26; Y, 14.86. $^1$H NMR ($C_6D_6$): 0.94 (s, 6H, $CH_3C{=}N$), 1.42 (s, 36H, $(C(CH_3)_3)$), 1.52 (s, 8H, THF), 2.11 (s, 6H, $CH_3C{=}O$), 2.29 (s, 12H, $CH_3$ (arene ring)), 3.64 (s, 8H, THF), 4.83 (s, 2H, CH), 7.00−7.10 (d, 4H, Ar), 7.15 (s, 2H, Ar), 7.20 (s, 4H, Ar). IR (KBr, $cm^{-1}$): 2959 (s), 2917 (m), 2870 (m), 1593 (s), 1493 (s), 1431 (s), 1362 (s), 1289 (m), 1157 (w), 1026 (w), 934 (w), 833 (w), 768 (w), 621 (w), 505 (w).

**Typical Procedure for the Polymerization Reaction.** The procedures for the polymerization of L-lactide initiated by complexes **6**−**9** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of L-lactide and toluene. The contents of the flask were then stirred at 70 °C until L-lactide was dissolved, and then a solution of the initiator in toluene was added to this solution by syringe. The mixture was stirred vigorously at 70 °C for the desired time, during which time an increase in the viscosity was observed. The reaction mixture was quenched by the addition of methanol and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

**X-ray Crystallography.** Suitable single crystals of complexes **2** and **4**−**6** were sealed in a thin-walled glass capillary for determination of the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in $\omega$ 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 2.

**Table 2.** Crystallographic Data for Complexes **2** and **4−6**

| compd | **2** | **(3 × 4)·2THF** | **(3 × 5)·2THF** | **6·2THF** |
|---|---|---|---|---|
| formula | $C_{80}H_{116}N_4Na_8O_{16}$ | $C_{104}H_{154}Cl_6N_6O_{26}Yb_6$ | $C_{104}H_{154}Cl_6N_6O_{26}Tb_6$ | $C_{70}H_{104}N_2Nd_2O_{10}$ |
| fw | 1573.69 | 3155.27 | 3070.55 | 1422.03 |
| $T$ (K) | 153(2) | 193(2) | 193(2) | 193(2) |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ |
| cryst size (mm) | 0.70 × 0.60 × 0.50 | 0.64 × 0.21 × 0.20 | 0.50 × 0.35 × 0.20 | 0.40 × 0.28 × 0.12 |
| $a$ (Å) | 22.279(2) | 13.0267(7) | 13.139(1) | 13.618(2) |
| $b$ (Å) | 15.674(1) | 14.9810(8) | 15.069(1) | 16.397(2) |
| $c$ (Å) | 24.110(2) | 31.474(2) | 31.425(3) | 16.292(2) |
| $\beta$ (deg) | 94.871(2) | 98.400(1) | 97.889(2) | 103.592(4) |
| $V$ (Å$^3$) | 8389.0(10) | 6076.3(6) | 6162.9(9) | 3536.1(8) |
| $Z$ | 4 | 2 | 2 | 2 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.246 | 1.725 | 1.655 | 1.336 |
| $\mu$ (mm$^{-1}$) | 0.120 | 4.770 | 3.593 | 1.506 |
| $F$(000) | 3360 | 3100 | 3040 | 1476 |
| $\theta_{max}$ (deg) | 25.35 | 27.48 | 27.48 | 25.35 |
| collected reflns | 80 444 | 60 491 | 56 812 | 34 173 |
| unique reflns | 15 293 | 13 873 | 13 954 | 6469 |
| obsd reflns [$I > 2.0\sigma(I)$] | 13 219 | 12 637 | 12 612 | 5435 |
| no. of variables | 986 | 658 | 658 | 385 |
| GOF | 1.084 | 1.105 | 1.128 | 1.227 |
| $R$ | 0.0566 | 0.0358 | 0.0387 | 0.0702 |
| w$R$ | 0.1341 | 0.0837 | 0.0916 | 0.1220 |
| largest diff peak, hole (e Å$^{-3}$) | 0.933, −0.448 | 1.630, −1.486 | 1.777, −1.364 | 1.214, −0.735 |

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. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement.

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**Supporting Information Available:** Crystallographic data for complexes **2** and **4−6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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