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Phenylene-bridged β-Ketoiminate Dilanthanide Aryloxides: Synthesis, Structure, and Catalytic Activity for Addition of Amines to Carbodiimides

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Abstract. The synthesis and reactivity of a series of bimetallic lanthanide aryloxides stabilized by a *p*-phenylene-bridged bis(β-ketoiminate) ligand is presented. The reaction of 1,4-diaminobenzene with acetylacetone in a 1:2.5 molar ratio in absolute ethanol gave the compound 1,4-bis(4-imino-2-pentanone)benzene (**1**) (LH_2) in high yield. Compound **1** reacted with $(ArO)_3Ln(THF)_2$ (ArO = 2,6-tBu$_2$-4-MeC_6H_2O, THF = tetrahydrofuran) in a 1:2 molar ratio in THF, after workup, to give the corresponding dilanthanide aryloxides $L[Ln(OAr)_2(THF)]_2$ [*Ln* = Yb (**2**), Y (**3**), Sm (**4**), Nd (**5**), La (**6**)] in high isolated yields. Compound **1** and complexes **2**–**6** were fully characterized, including X-ray crystal structure analyses for complexes **2**, **3**, **5**, and **6**. Complexes **2**–**6** can be used as efficient pre-catalysts for catalytic addition of amines to carbodiimides, and the ionic radii of the central metal atoms have a significant effect on the catalytic activity with the increasing sequence of La (**6**) < Nd (**5**) ≈ Sm (**4**) < Y (**3**) ≈ Yb (**2**). The catalytic addition reaction with **2** showed a good scope of substrates including primary and secondary amines.

Introduction

β-Diketiminate monoanions, as one of the significantly important non-cyclopentadienyl ancillary ligands, have received increasing attention in organometallic chemistry of lanthanide metals.[1] Various lanthanide complexes (alkyls, amides, alkoxides etc.) stabilized by β-diketiminate ligands have been synthesized and structurally characterized.[2,3] Moreover, these derivatives have been found to be efficient catalysts or pre-catalysts in organic and polymerization reactions,[4] and also exhibit versatile reactivity, such as activation of small molecules, reduction by alkali metal, oxidation, deprotonation, etc.[5] β-Ketoiminate anions can be viewed as the counterparts of β-diketiminate anions. These monoanions, as ancillary ligands in organometallic chemistry, also own similar attractive features: they can be facilely prepared with readily and inexpensive starting materials;[6] the steric and electric effects can be easily modulated by adjusting the substituent on the nitrogen atom;[7] they display strong coordination ability to the central metal as bidentate monoanionic ligands, which have been viewed as excellent heteroatom analogues of pentadienyl ligands.[8] Besides, their binding to the metal center can lead to a six-membered ring and cause the metal atom surrounded by a bulky substituent on one side but left the other side open, thus resulting in ligand hemilability and potentially interesting catalytic behavior.[6a,9] However, the application of ketoiminate anions as ligands in organolanthanide chemistry has been much less explored in comparison with their counterparts β-diketiminate anions.[10] The first monomeric and solvent-free homoleptic ytterbium tris(β-ketoiminate) complex was prepared by *Rees*.[10i] Next, a series of $(CH_2)_3$-bridged lanthanide β-ketoiminate complexes were intensively investigated by the *Belot* group, including amido and aryloxo complexes,[10d,10e,10h] and a drastical impact of lanthanide metal radii on the composition and molecular structure of the isolated complexes has been pointed out.[10e,10h] In 2002, *Edleman* et al. developed monomeric lanthanide complexes supported by β-ketoiminate ligand. They demonstrated that these complexes could be used as excellent MOCVD precursors.[10f] Our group presented the synthesis and reactivity of lanthanide complexes supported by *N*-aryloxo-functionalized β-ketoiminate ligand.[10a] Obviously, further development of novel β-ketoiminate ligands and exploring their application in organolanthanide chemistry is certainly required.

Recently, a great attention has been paid to the construction of C–N bonds, which is of great importance in organic synthesis, by organometallic complexes as the catalysts or pre-catalysts.[11] The catalytic formation of guanidine by addition of amine and carbodiimide is especially an active arena as this offers a straightforward and atom-economical route for the preparation of multi-substituted guanidines, which play a vital role in many biological and pharmaceutical compounds.[12] Various organolanthanide complexes including alkyl and amide derivatives were proven to be excellent catalysts for this transformation.[13] We have recently addressed that homoleptic

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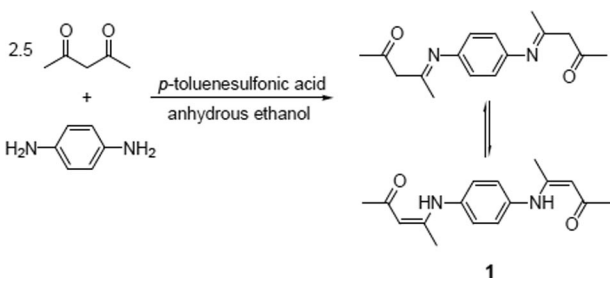
lanthanide trisaryloxides could also serve as excellent pre-catalysts.[14] The lanthanide aryloxides supported by a bridged-amidinate[15] or by a β-diketiminate ligand[4a] are also efficient pre-catalysts. Lanthanide aryloxides are robust and easier to be treated than lanthanide alkyl and amide complexes. Thus, further development of novel lanthanide aryloxide catalysts is of interest. To continue our study and to explore the application of β-ketoiminate ligands in lanthanide chemistry, we are interested in development of novel β-ketoiminate ligands and lanthanide aryloxides with them, and exploit their potential catalytic behavior. In this work, a novel phenylene-bridged bis(β-ketoiminate) ligand, 1,4-bis(4-imino-2-pentanone)benzene (**1**) (LH_2) was developed and a series of bimetallic lanthanide aryloxides L[*Ln*$(OAr)_2(THF)]_2$ [*Ln* = Yb (**2**), Y (**3**), Sm (**4**), Nd (**5**), La (**6**)] were synthesized and fully characterized. The catalytic activity of these aryloxides as pre-catalyst towards amines and carbodiimides addition giving guanidines and the possible reaction pathway are also addressed.

Results and Discussion

Synthesis and Characterization of Compound 1

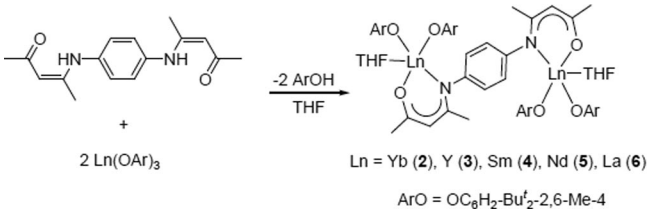
The reaction of a mixture of 1,4-diaminobenzene with 2.5 equiv. of 2,4-pentanedione in absolute anhydrous ethanol in the presence of catalytic amount of *p*-toluenesulfonic acid under reflux condition afforded the novel *p*-phenylene-bridged bis(β-ketoiminate) ligand LH_2 (**1**) [L = *p*-OC(Me)CHC(Me)N-C_6H_4-*p*-NC(Me)CHC(Me)O] as a raw product. After recrystallization from ethanol, pure **1** was obtained in a satisfactory yield (85%) (Scheme 1). The merit of this method is that the available and inexpensive 1,4-diaminobenzene was used as a starting material. Compound **1** was comprehensively characterized by NMR spectroscopy, IR spectroscopy as well as elemental analysis. ^{1}H NMR spectrum of **1** reveals the methine proton of the ketoiminate backbone at δ = 5.20 ppm, which is consistent with analogous bridged bis(β-ketimine) ligand linked by 4,4′-methylene-bis(2–6-diisopropylaniline),[6b] and diaminocyclohexane.[6a,6c]



Scheme 1. Synthesis of compound **1**.

Synthesis and Characterization of Complexes 2–6

Ligand exchange is an effective strategy for the synthesis of various lanthanide complexes. Thus, the lanthanide triaryloxide complex was used here as a starting material and its reaction with **1** was tried in order to explore an facile route for the synthesis of lanthanide aryloxides stabilized by a *p*-phenylene-bridged bis(β-ketoiminate) ligand. The reaction of $(ArO)_3Yb(THF)_2$ [ArO = 2,6-*t*Bu_2-4-MeC_6H_2O] with **1** was first conducted at a molar ratio of 2 to 1 in THF. The reaction went smoothly at room temperature. Stirring 24 h afforded a clear yellow solution, from which a bimetallic ytterbium aryloxide bearing one L ligand L[$Yb(OAr)_2(THF)]_2$ (**2**) was isolated in 76% yield. Further study demonstrated that this procedure is suitable for the synthesis of the lanthanide metal complexes including the early metals of La (**6**), Nd (**5**), middle metal of Sm (**4**), and the metal Y (**3**). All these complexes were facilely isolated as crystals in high yields (Scheme 2). However, an attempt for the synthesis of a bimetallic lanthanide monoaryloxide bearing two L ligands by the reaction of $[Yb(OAr_3)THF)_2]$ with equiv. of L was unsuccessful. The reaction afforded a gel, which is difficult to be treated further. Complexes **2–6** are sensitive to air and moisture. They are moderately soluble in THF and toluene, but poorly soluble in hexane.



Scheme 2. Synthesis of complexes **2–6**.

All these novel aryloxide complexes were fully characterized by elemental analysis and IR spectroscopy. The elemental analyses of complexes **2–6** are consistent with their formulae. Their IR spectra exhibit strong absorptions near 1622, 1609, 1605, 1566, 1559 cm^{-1}, respectively, which are consistent with the characteristic of partial C=N bond of the β-ketoiminate ligands.[6,7a,10a] The ^{1}H NMR spectra of the diamagnetic complexes **3** and **6** in C_6D_6 show the expected sets of signals assigned to the L, ArO, and the coordinated THF molecule.[14]

To provide comprehensively structural information complexes **2**, **3**, **5**, and **6** were further confirmed by a X-ray single-crystal structure analysis (crystal structure of complex **4** was not determined for its deterioration in the crystal quality). Suitable crystals were obtained by cooling a toluene solution at 0 °C for **2**, **4**, and **5**, and by cooling a THF solution at 0 °C for **3** and **6**. Each complex has several free THF molecules in its unit cell (**5**: toluene molecule in its unit cell), and these free solvent molecules are entirely lost under vacuum. Therefore, the elemental analysis data for each complex is well consistent with the formula without the free solvent molecules.

Complexes **2**, **3**, **5**, and **6** are isostructural. Their molecular structures are shown in Figure 1 and the selected bond lengths and angles are listed in Table 1. Each complex is a THF-solvated monomer. They have a centrosymmetric structure with the symmetric center on phenyl ring of the bridge. Each molecule contains two metals and each metal atom coordinated

Table 1. Selected bond lengths /Å and angles /° for complexes **2**, **3**, **5**, and **6**.

	2	**3**	**5**	**6**
Ln(1)–O(1)	2.098(3)	2.137(3)	2.213(10)	2.291(2)
Ln(1)–O(2)	2.075(3)	2.113(3)	2.190(9)	2.242(2)
Ln(1)–O(3)	2.080(3)	2.125(3)	2.191(9)	2.253(2)
Ln(1)–O(4)	2.340(3)	2.374(3)	2.520(11)	2.585(3)
Ln(1)–N(1)	2.348(3)	2.396(3)	2.489(10)	2.561(3)
O(1)–C(2)	1.303(5)	1.297(5)	1.286(17)	1.294(5)
C(2)–C(3)	1.363(6)	1.358(6)	1.436(19)	1.362(5)
C(3)–C(4)	1.420(6)	1.430(6)	1.428(18)	1.430(5)
N(1)–C(4)	1.325(5)	1.308(5)	1.314(16)	1.314(4)
O(1)–*Ln*(1)–O(2)	108.01(12)	103.54(11)	106.8(4)	107.86(9)
O(2)–*Ln*(1)–O(3)	147.97(12)	147.03(10)	147.5(3)	142.38(8)
O(3)–*Ln*(1)–O(1)	103.20(12)	108.81(11)	105.0(4)	108.39(9)
N(1)–*Ln*(1)–O(4)	161.34(12)	159.49(11)	159.2(3)	151.59(10)

to one nitrogen atom and one oxygen atom from the L ligand, two oxygen atoms from the two aryloxido groups and one oxygen atom from the THF molecule. The coordination arrangement surrounding each metal atom can be described as a distorted trigonal bipyramid. The two oxygen atom of aryloxido, and the oxygen atom of the β-ketoiminate ligand form the equatorial vertices. The sum of three bond angles of 359.18(12), 359.38(11), 359.3(4), 358.63(9)° for **2**, **3**, **5**, and **6**, respectively, slightly deviates from ideal 360°. The nitrogen atom N(1) of the β-ketoiminate ligand and the oxygen atom O(4) of the THF occupy the apical positions with the angle of N(1)–*Ln*–O(4) of 161.34(12)° (**2**), 159.49(11)° (**3**), 159.2(3)° (**5**), and 151.59(10)° (**6**), respectively, which significantly deviates from the ideal 180°. The two aryloxido groups located at the opposite sites. This may be attributed to the steric hindrance. The molecular structures of the present complexes are quite similar to that of $(CH_2)_3$-bridged tetradentate bis(β-ketoiminate) lanthanide complexes reported previously.[10d,10e]

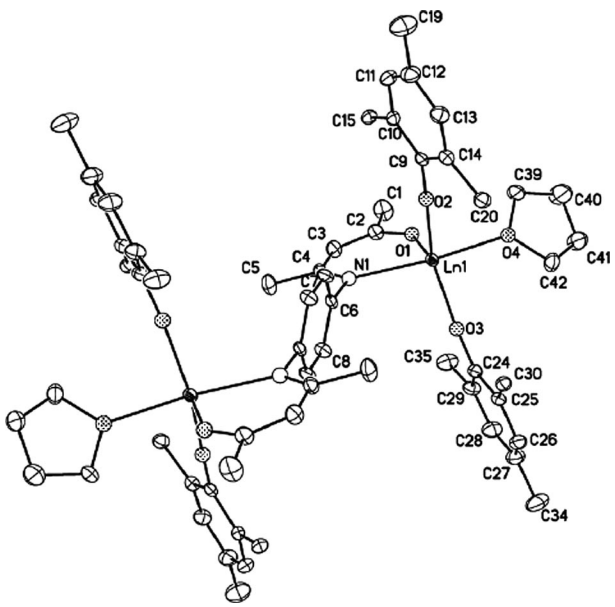


Figure 1. ORTEP diagram of L[*Ln*$(OAr)_2$(THF)$]_2$ [*Ln* = Yb (**2**), Y (**3**), Nd (**5**), La (**6**)] showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

The bond lengths of central metal atoms to the L ligand including the bonds of *Ln*–O (alkoxo) and *Ln*–N {[2.098(3) and 2.348(3) Å] (**2**), [2.137(3) and 2.396(3) Å] (**3**), [2.213(10) and 2.489(10) Å] (**5**), and [2.291(2) and 2.561(3) Å] (**6**), respectively} can be compared to those found in the ytterbium bidentate β-ketoiminate complex L′$_3$Yb [L′ = *t*BuCOCHC(*t*Bu)N(*n*Pr)] (Yb–O = 2.15, 2.15, 2.16 Å; Yb–N = 2.38, 2.44, 2.44 Å),[10i] and the ytterbium tridentate β-ketoiminate complex [L′′*Ln*Cl(DME)]$_2$ (L′′ = [MeCOCHC(Me)NC$_6$H$_4$O(4-Me)]$^{2-}$) [Yb–O = 2.140(4) Å, Yb–N = 2.399(4) Å],[10a] when the influences of the coordination number and the ion radium of the central metal atoms were considered, revealing a similar π electron delocalization present within (OCCCN) backbone in complexes **2**, **3**, **5**, and **6**.

The two *Ln*(1)–O(aryloxo) bond lengths are basically equivalent [2.075(3) and 2.080(3) Å for **2**; 2.113(3) and 2.125(3) Å for **3**; 2.190(9) and 2.191(9) Å for **5**; 2.242(2) and 2.253(2) Å for **6**], which reflect the coordination mode of metal to each of the oxygen atom of aryloxido is same. All the bond parameters of complexes **2**, **3**, **5**, and **6** including the bonds of metal to L and to aryloxo groups are well comparable with each other, when the differences in the ion radii among these metals are considered.

Catalytic Activity of 2–6 for Additions of Amines to Carbodiimides

Only one example regarding the catalytic behavior of lanthanide β-ketoiminate complex for polar monomer polymerization has been reported to date.[10a] Thus, the catalytic activity of complexes **2**–**6** for catalytic addition of amines to carbodiimides to guanidines was evaluated. The reaction of $PhNH_2$ with *N*,*N*′-diisopropylcarbodiimide (*i*PrNCN*i*Pr), as the model reaction, was performed at 60 °C under solvent free condition for 0.25 h in the presence and the absence of complex **2**, respectively. The results are listed in Table 2. It's clear that the reaction did not take place without the presence of complex **2** (Table 2, entry 1). In contrast, the reaction occurred immediately to yield the corresponding guanidine **7** in almost a quantitative yield when 0.5 mol% of complex **2** was added (Table 2, entry 2). Complexes **3**–**6** all can serve as catalyst precursors

for this catalytic reaction to afford product **7**. However, the yield of **7** varies greatly. For example, the reaction with complexes **2** and **3** afforded **7** in 98% and 94% isolated yield, respectively, whereas the yields were 51%, 49% and 20%, respectively, when complexes **4**, **5**, and **6** were used (Table 2, entries 2–6). The active sequence of La (**6**) < Nd (**5**) ≈ Sm (**4**) < Y (**3**) ≈ Yb (**2**) found herein is in accordance with the decrease of radii of the central metals. Such a dependence of the activity on the metal size has also been found in the reported systems with lanthanide aryloxide.[15] Complex **2** is a highly active pre-catalyst and the reaction can still afford **7** in 33% yield after a short time period (0.25 h) even when the amount of complex **2** decreased to 0.1 mol% (Table 2, entry 7).

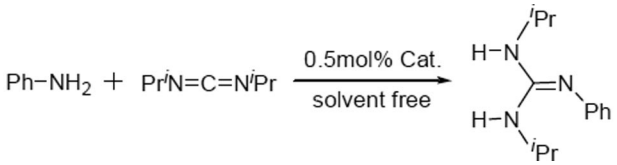


Table 2. Addition of $PhNH_2$ to *i*PrNCN*i*Pr by complexes **2**–**6**.[a]

Entry	Cat.	Temp. /°C	Time /h	Yield [b] /%
1	–	60	0.25	0
2	**2**	60	0.25	98
3	**3**	60	0.25	94
4	**4**	60	0.25	51
5	**5**	60	0.25	49
6	**6**	60	0.25	20
7 [c]	**2**	60	0.25	33

a) Aniline (1.6 mmol), *N*,*N*′-diisopropylcarbodiimide (1.6 mmol). b) Isolated yields. c) 0.1 mol% catalyst loading.

To see the generality of the present pre-catalysts for catalytic syntheses of substituted guanidines, the catalytic addition of various primary and secondary amines to carbodiimides was then examined using complex **2**. Representative results are summarized in Table 3. As shown in Table 3, complex **2** is a very robust and efficient pre-catalyst. The system is compatible with a wide range of substituents at the phenyl ring of the aromatic amines, regardless of the electron-withdrawing or electron-donating groups. Primary and secondary amines both could be used for this reaction. However, the reaction with a bulky amine, 2,6-diisopropylaniline, is less efficient, affording the guanidine in only a 64% yield, even prolong reaction period to 24 h (Table 3, entry 14). This might be because of the larger steric hindrance of the substrate. The similar situation was also documented in the published work.[4a,15,16] The reaction with secondly aliphatic amines, such as pyrrolidine and piperidine, also requires prolong the reaction time from 0.5 h to 24 h, to deliver the relevant guanidines (**21** and **22**) in good yields (Table 3, entries 15 and 16). This may be attributed to their less active, compared to the primary aromatic amines. Thus, the catalytic behavior of the present lanthanide aryloxide complexes can be well comparable with the lanthanide aryloxide complexes including triaryloxides[14] and the aryloxides stabilized by β-diketiminate[4a] and bridged amidinate ligands reported previously.[15]

To better understand the reaction pathway of the present catalytic cycle, a NMR tube reaction with stoichiometric amount of **3** and $PhNH_2$ was measured. The slowly increasing signal at δ = 4.79 ppm during the whole detection period was observed. The new signal may be assigned to the OH proton of the released 2,6-*t*Bu_2-4-MeC_6H_2OH. The appearance of free 2,6-*t*Bu_2-4-MeC_6H_2OH indicated that the protonation reaction

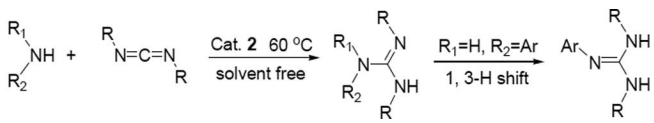
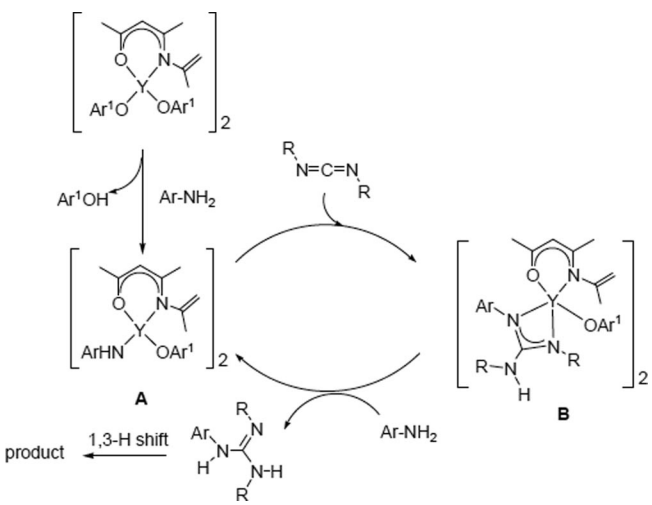


Table 3. Catalytic addition of amines to carbodiimides.[a]

Entry	*R*	R_1R_2NH	Catalyst loading /mol%	Time /h	Product	Yield [b] /%
1	*i*Pr	Ph-NH_2	0.5	0.5	**7**	>99
2	Cy		0.5	0.5	**8**	96
3	*i*Pr	*p*-F-Ph-NH_2	0.5	0.5	**9**	>99
4	Cy		0.5	0.5	**10**	99
5	*i*Pr	*o*-Cl-Ph-NH_2	0.5	0.5	**11**	>99
6	Cy		0.5	0.5	**12**	90
7	*i*Pr	*o*-Me-Ph-NH_2	0.5	1.0	**13**	93
8	Cy		0.5	1.0	**14**	93
9	*i*Pr	*p*-Me-Ph-NH_2	0.5	0.5	**15**	95
10	*i*Pr	*p*-Cl-Ph-NH_2	0.5	0.5	**16**	>99
11	*i*Pr	*p*-Br-Ph-NH_2	0.5	0.5	**17**	>99
12	*i*Pr	*p*-MeO-Ph-NH_2	0.5	2	**18**	98
13	*i*Pr	1-naPh-NH_2	0.5	24	**19**	94
14	*i*Pr	2,6-*i*Pr_2-Ph-NH_2	0.5	24	**20**	64
15	*i*Pr	*cyclo*-C_4H_8NH	0.5	24	**21**	83
16	*i*Pr	*cyclo*-$C_5H_{10}NH$	0.5	24	**22**	95

a) The reaction was performed by treating 1 equiv. of amines with 1 equiv. of carbodiimides at 60 °C. b) Isolated yields.

of complex **3** with aniline occurred to form the intermediate amido species. Also, the new signals at δ = 0.89 and 3.48 ppm, which may be assigned to the corresponding Y-guanidinate species formed, were detected, when an equiv. of *i*PrNCN*i*Pr was added. The formation of the Y-guanidinate species indicates the nucleophilic addition of an *Ln*–N bond newly formed to a carbodiimide compound then took place. The similar transformations have been addressed in our recent work.[4a] According to the NMR experimental data the possible catalytic pathway is depicted in Scheme 3. At first, amination of complex **3** by aniline afforded the intermediate **A**. Then, the nucleophilic addition of **A** to a carbodiimide yielded the active species **B**. The protonolysis of **B** by aniline gave the product guanidine and release **A** to complete the catalytic cycle. An attempt to isolate the real active species **A** and **B** was unsuccessful.



Scheme 3. Possible pathway of catalytic addition of amines to carbodiimides.

Conclusions

In this paper, we have developed a phenylene-bridged bis(β-ketoiminate) proligand. A series of bridged bis(β-ketoiminate) dilanthanide aryloxides stabilized by this ligand was synthesized via ligand exchange reaction using $Ln(OAr)_3(THF)_2$ as a synthon. Their structural features were determined by X-ray diffraction experiments. These novel β-ketoiminate lanthanide aryloxides exhibit good activity for the catalytic addition of amines to *N*,*N*′-dialkylcarbodiimide to substituted guanidines with the active sequence of La (**6**) < Nd (**5**) ≈ Sm (**4**) < Y (**3**) ≈ Yb (**2**). Further study on design and synthesis of new bis(β-ketoiminate) lanthanide derivatives are in process.

Experimental Section

General Procedures: All manipulations were performed in pure argon atmosphere with rigorous exclusion of air and moisture using the standard Schlenk techniques. Solvents of THF, toluene and *n*-hexane were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. [D_6]Benzene was dried with fresh sodium chips in the glovebox for NMR reactions. Carbodiimides and amines were purchased from TCI and were used as supplied. NaOAr was prepared from the reaction of ArOH with Na in THF. $(ArO)_3Ln(THF)_2$ was prepared according to a literature procedure.[17] ^{1}H NMR and ^{13}C NMR spectra were run with a Bruker DPX-300 or a Unity Inova-400 spectrometer. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer. Elemental analyses were performed by direct combustion with a Carlo-Erba EA 1110 instrument. The Infrared spectra were recorded with a Magna-IR 550 spectrometer as KBr pellets. The uncorrected melting points of crystalline samples in sealed capillaries (in argon) are reported as ranges.

Synthesis of the Proligand LH_2 (1): To a solution of 2,4-pentanedione (45.0 mL, 0.44 mol) in absolute anhydrous ethanol (250 mL) was added 1,4-diaminobenzene (19.5 g, 0.18 mol) and a catalytic amount of *p*-toluenesulfonic acid at room temperature. After the reaction mixture was stirred in oil bath and refluxed for 24 h under ambient condition, a red-brown liquid and a pale yellow solid were formed. This solid was separated by filtered, recrystallized from anhydrous ethanol and dried under vacuum. (41.6 g, 85 %); m.p. 180.3–180.8 °C. $C_{16}H_{20}N_2O_2$ (272.34): calcd. C 70.56; H 7.40; N 10.29 %; found: C 70.31; H 7.41; N 10.42 %. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.47 (s, 2 H, N*H*), 7.08 (s, 4 H, Ar*H*), 5.20 [s, 2 H, C*H*=C(CH$_3$)N], 2.11 (s, 6 H, CH_3), 2.01 (s, 6 H, CH_3) ppm. **^{13}C NMR** (400 MHz, $CDCl_3$): δ = 196.4 (C=O), 160.0 (C–N), 136.2 (C_{aryl}), 125.2 (CH_{aryl}), 98.0 [C(N)–CH–C(N)], 29.3(CH_3), 19.9(CH_3) ppm. **IR** (KBr): $\tilde{\nu}$ = 3643 (s), 3450 (s), 2956 (s), 2871 (m), 1613 (s), 1567 (vs), 1497 (s), 1436 (vs), 1358 (s), 1235 (s), 1158 (s), 1119(m), 1027 (m), 864 (m), 772 (m), 741 (m), 625 (m), 571 (m) cm^{-1}.

L[Yb(OAr)$_2$(THF)]$_2$ (2): A THF (20 mL) solution of LH_2 (0.60 g, 2.20 mmol) was added slowly to a $(ArO)_3Yb(THF)_2$ (4.40 mmol) in THF (20 mL) at room temperature. After stirring for 24 h, the transparent orange yellow solution was evaporated in vacuo, and the solid residue extracted with toluene. After the undissolved portion was removed by centrifugation, the yellow solution was concentrated. Crystallization at 0 °C for a week afforded **2** as orange yellow crystals (2.98 g, 76 %); m.p. 125 °C (decomp.). $C_{84}H_{126}N_2O_8Yb_2$ (1637.95): calcd. C 61.60; H 7.75; N 1.71; Yb 21.13 %; found C 61.43; H 7.88; N 1.65; Yb 21.05 %. **IR** (KBr): $\tilde{\nu}$ = 3639 (m), 3432 (m), 2957 (s), 1609 (vs), 1518 (s), 1435 (vs), 1362 (s), 1310 (s), 1273 (vs), 1229 (s), 1157 (s), 1119 (m), 1026 (s), 921 (w), 861 (m), 770 (m), 624 (m), 503 (m) cm^{-1}.

L[Y(OAr)$_2$(THF)]$_2$ (3): The synthesis of complex **3** was carried out in the same way as that described for complex **2**, but $(ArO)_3Y(THF)_2$ (4.22 mmol) was used instead of $(ArO)_3Yb(THF)_2$. Colorless crystals were obtained from THF at 0 °C (2.79 g, 70 %); m.p. 143 °C (decomp.). $C_{84}H_{126}N_2O_8Y_2$ (1469.75): calcd. C 68.65; H 8.64; N 1.91; Y 12.10 %; found: C 68.23; H 8.75; N 1.93; Y 12.02 %. **^{1}H NMR** (400MHz, C_6D_6): δ = 7.22 (s, 8 H, Ar*H*), 7.12 (s, 4 H, Ar*H*), 5.16 [s, 2 H, C*H*=C(CH$_3$)N], 2.39 (s, 12 H, ArCH_3), 1.89 (s, 6 H, CH_3), 1.65 (s, 6 H, CH_3), 1.51 (s, 72 H, *t*Bu) ppm. **^{13}C NMR** (400MHz, C_6D_6): δ = 177.9, 160.7, 143.8, 138.4, 126.2, 125.9, 124.2, 103.5, 67.7, 35.2, 31.6, 30.4, 26.2, 23.6, 23.1, 21.6, 14.4. **IR** (KBr): $\tilde{\nu}$ = 3640 (m), 3439 (s), 2960 (m), 1622 (vs), 1564 (s), 1505(m) 1450 (m), 1391 (vs), 1381 (vs), 1274 (m), 1224 (m), 1158 (s), 1123 (m), 998 (w), 880 (m), 773 (m), 624 (m), 421 (m) cm^{-1}.

L[Sm(OAr)$_2$(THF)]$_2$ (4): The synthesis of complex **4** was carried out in the same way as that described for complex **1**, but $(ArO)_3Sm(THF)_2$ (4.64 mmol) was used instead of $(ArO)_3Yb(THF)_2$. Pale yellow crystals were obtained from toluene at 0 °C (2.84 g, 65 %);

m.p. 152 °C (decomp.). $C_{84}H_{126}N_2O_8Sm_2$ (1592.65): calcd. C 63.35; H 7.97; N 1.76; Sm 18.88%; found: C 63.55; H 8.05; N 1.67; Sm, 18.89%. **IR** (KBr): $\tilde{\nu}$ = 3621 (m), 3464 (m), 2958 (s), 1611 (s), 1566 (vs), 1470 (s), 1435 (s), 1309 (s), 1271 (s), 1232 (s), 1157 (s), 1119 (s), 1028 (s), 865 (m), 772 (m), 743 (m) cm^{-1}.

L[Nd(OAr)$_2$(THF)]$_2$ (5): The synthesis of complex **5** was carried out in the same way as that described for complex **1**, but $(ArO)_3Nd(THF)_2$ (3.12 mmol) was used instead of $(ArO)_3Yb(THF)_2$. Pale green crystals were obtained from toluene at 0 °C (1.89 g, 72%); m.p. 155 °C (decomp.). $C_{84}H_{126}N_2O_8Nd_2$ (1580.41): calcd. C 63.84; H 8.04; N 1.77; Nd 18.25%; found: C 64.12; H 8.20; N 1.75; Nd 18.32%. **IR** (KBr): $\tilde{\nu}$ = 3643 (m), 3419 (s), 2964 (s), 2917 (m), 2871 (m), 1605 (s), 1566 (s), 1520 (s), 1436 (s), 1389 (s), 1312 (s), 1227 (vs), 1158 (vs), 1027 (m), 926 (w), 864 (m), 772 (m), 633 (m), 556 (m), 509 (m) cm^{-1}.

L[La(OAr)$_2$(THF)]$_2$ (6): The synthesis of complex **6** was carried out in the same way as that described for complex **1**, but $(ArO)_3La(THF)_2$ (4.88 mmol) was used instead of $(ArO)_3Yb(THF)_2$. Colorless crystals were obtained from THF at 0 °C (3.84 g, 85%); m.p. 173 °C (decomp.). $C_{84}H_{126}N_2O_8La_2$ (1569.74): calcd. C 64.27; H 8.09; N 1.78; La 17.70%; found: C 64.20; H 8.21; N 1.74; La 17.80%. **^{1}H NMR** (400 MHz, C_6D_6): 7.18 (s, 12 H, Ar*H*), 5.09 [s, 2 H, C*H*=C(CH$_3$)N], 2.43 (s, 12 H, ArCH_3), 1.90 (s, 6 H, CH_3), 1.63 (s, 6 H, CH_3), 1.52 (s, 72 H, *t*Bu) ppm. **^{13}C NMR** (400MHz, C_6D_6): δ = 178.4, 170.1, 162.2, 137.7, 136.0, 125.9, 125.7, 125.6, 123.7, 68.6, 34.8, 34.4, 31.2, 31.0, 30.5, 26.5, 25.6, 23.0, 21.8. **IR** (KBr): $\tilde{\nu}$ = 2995 (s), 1945 (m), 1559 (vs), 1520 (vs), 1436 (s), 1358 (s), 1312 (vs), 1273 (vs), 1227 (s), 1189 (s), 1027 (s), 918 (s), 864 (s), 803 (2), 764 (s), 625 (s), 571 (m), 540 (m), 509 (m) cm^{-1}.

General Procedure for the Reaction of Amines with Carbodiimides Catalyzed by Complex 2: A 10 mL Schlenk tube in a dried argon atmosphere was charged with **2** (14.2 mg, 0.008 mmol). To the flask were added the aniline ($PhNH_2$) (0.146 mL, 10.96 M, 1.60 mmol), *N*,*N*′-diisopropylcarbodiimide (*i*PrNCN*i*Pr) (0.249 mL, 6.418 M, 1.60 mmol). The resulting mixture was stirred at 60 °C for the desired time, as shown in Table 3. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with dichloromethane (3 × 10 mL), dried with anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the final products were further purified by crystallization from *n*-hexane (0.344 g, 98% yield).

X-ray Crystallography: Crystals suitable for X-ray diffraction of complexes **2**, **3**, **5**, and **6** were sealed, respectively, in a thin-walled glass capillary filled with argon for structural analysis. Diffraction data were collected with a Bruker APEX-II CCD area detector in the ω scan mode using Mo-K_α radiation (λ = 0.71070 Å) for complexes **2** and **6**, with a Agilent Xcalibur CCD area detector in the ω scan mode using Mo-K_α radiation (λ = 0.71073 Å) for complex **3**, and with a Rigaku Saturn CCD area detector in the ω scan mode using Mo-K_α radiation (λ = 0.71075 Å) for complex **5**. 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 4. 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 calculations in the final stage of full-matrix least-squares refinement. The structures were refined using SHELEXL-97 programs.[18]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1030495 (for **2**), CCDC-1030496 (for **3**), CCDC-1030498 (for **5**) and CCDC-1030499 (for **6**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Spectroscopic data for the addition products of amines to carbodiimides.

Table 4. Crystallographic data for complexes **2**, **3**, **5** and **6**.

	2·2thf	**3**·6thf	**5**·toluene	**6**·4thf
Empirical formula	$C_{92}H_{142}N_2O_{10}Yb_2$	$C_{108}H_{174}N_2O_{14}Y_2$	$C_{91}H_{134}N_2O_8Nd_2$	$C_{100}H_{158}N_2O_{12}La_2$
Formula mass	1782.16	1902.31	1672.48	1858.10
T /K	193(2)	223(2)	223(2)	153(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a /Å	16.8447(15)	13.3209(8)	17.768(6)	12.7859(13)
b /Å	16.6286(15)	15.2897(7)	15.282(4)	13.1457(13)
c /Å	17.1105(16)	15.3594(11)	18.636(5)	15.6279(13)
α /°	90	100.057(5)	90	75.040
β /°	102.498(3)	107.043(6)	105.867(8)	76.787(4)
γ /°	90	106.911(5)	90	88.052(6)
V /Å^3	4679.1(7)	2743.7(3)	4867(2)	2469.6(4)
Z	2	1	2	1
$D_{calcd.}$ /g·cm^{-3}	1.265	1.151	1.141	1.249
μ /mm^{-1}	2.039	1.110	1.102	0.910
F(000)	1856	1026	1756	982
θ range /°	3.08–25.35	2.89–25.05	3.11–25.05	3.08–25.35
Reflns. collected	45675	23444	22197	24269
Reflns. observed [$I > 2\sigma(I)$]	7457	6340	3759	8382
Data/restraints/parameters	8542/12/490	9725/6/584	8520/325/490	8990/10/527
Goodness of fit on F^2	1.138	0.993	1.032	1.090
Final R [$I > 2\sigma(I)$]	0.0408	0.0662	0.1165	0.0392
wR_2 (all data)	0.0891	0.1320	0.3078	0.0947

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