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Synthesis and Characterization of Organolanthanide Complexes with a Calix[4]-pyrrolyl Ligand and Their Catalytic Activities toward Hydrophosphonylation of Aldehydes and Unactivated Ketones

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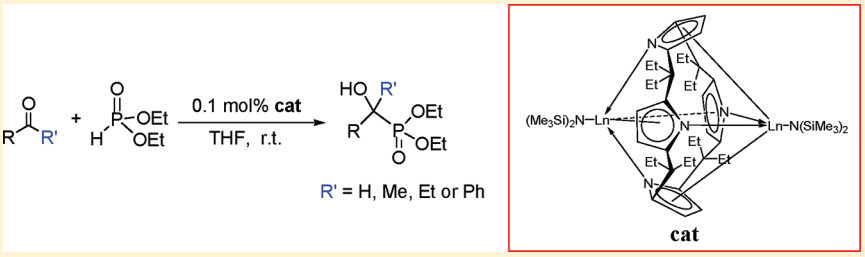
Supporting Information



ABSTRACT: The alkali metal salt free dinuclear trivalent lanthanide amido complexes (η^5:η^1:η^5:η^1-Et$_8$-calix[4]-pyrrolyl){LnN(SiMe$_3$)$_2$}$_2$ (Ln = Nd (**2**), Sm (**3**), Gd (**4**)) were prepared through the silylamine elimination reactions of calix[4]-pyrrole [Et$_2$C(C$_4$H$_2$NH)]$_4$ (**1**) with 2 equiv of [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ (Ln = Nd, Sm, Gd) in toluene at 110 °C. The complexes were fully characterized by elemental, spectroscopic, and single-crystal X-ray analyses. Studies on the catalytic activity of the new lanthanide amido complexes revealed that these complexes can be used as efficient catalysts for hydrophosphonylation of aldehydes and unactivated ketones, affording the products in high yields by employing a low catalyst loading (0.1 mol %) at room temperature in a short time (20 min). Noteworthy is that it is the first application of calix[4]-pyrrolyl-supported lanthanide amides as catalysts to catalyze the hydrophosphonylation of aldehydes and unactivated ketones under mild conditions.

INTRODUCTION

The employment of the calix[4]-pyrrolyl ligand is particularly appropriate for the high coordination numbers of lanthanide metals and hard donor atoms.[1] Each pyrrolyl anion can not only bond with metal in an η^5 or η^3 bonding mode through π electrons but also coordinate to lanthanide ions through lone-pair electrons of the nitrogen atom of the pyrrolyl ring. The divalent lanthanide complexes containing calix[4]-pyrrolyl ligands have been widely synthesized and applied in small molecule activation, such as reduction of N_2 or reversible fixation of ethylene.[2] However, the preparation of trivalent lanthanide complexes with calix[4]-pyrrolyl tetra-anion ligands usually resulted in a combination of the alkali metal salts through the metathesis reaction.[3] To avoid the combination of alkali metal salts in these complexes, the *N*-methyl substituents of the calix[4]-pyrrole has been introduced to lanthanide chemistry for the synthesis of the mononuclear calix[4]-pyrrolyl lanthanide amido complexes.[4] More recently, we have also reported that the alkali-metal-free bent-sandwich lanthanide amido complexes with Me$_8$- or {-(CH$_2$)$_5$-}$_4$-calix[4]-pyrrolyl ligands could be obtained through the direct silylamine elimination reaction of the corresponding calix[4]-pyrroles with lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$; these complexes showed good controllability on the ring-opening polymerization of L-lactide.[5]

The development of an efficient method for the synthesis of α-hydroxy phosphonates has become a field of interest due to their potential biological activities.[6] The direct addition of dialkyl phosphites to carbonyl compounds (Pudovik reaction) is an efficient way for the synthesis of α-hydroxy phosphonates with good selectivity and high atomic efficiency.[7] Various metal complexes, including aluminum,[8] titanium,[9] lanthanide,[10] niobium,[11] and molybdenum complexes,[12] have been demonstrated to be the effective catalysts for hydrophosphonylation of aldehydes. However, ketones remain a challenging class of substrates for the hydrophosphonylation reaction, because they display a low reactivity toward dialkyl phosphites compared with aldehydes.[13] Indeed, there have been few reports on the base-catalyzed addition of dialkyl phosphites to ketones for the

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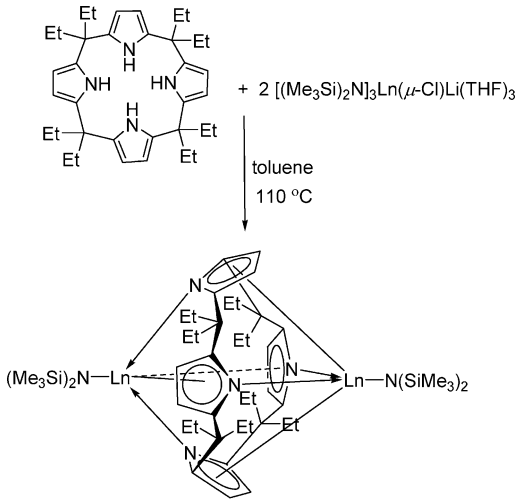
synthesis of quaternary α-hydroxy phosphonates, but the yields were not always good and mixtures of products were sometimes obtained due to the side reactions.[14] Recently, Feng and coworkers reported the first highly efficient Lewis acid catalyzed hydrophosphonylation of acetophenones and trifluoromethyl ketones by using $Ti(O^iPr)_4$[15] or Et_2AlCl[16] as catalysts. Despite these achievements, in view of the great utility of this hydrophosphonylation of unactivated ketones, the development of alternative efficient catalytic systems is still highly desirable. To further explore the application of lanthanide complexes as catalysts for such hydrophosphonylation of carbonyls, we herein report the synthesis and characterization of the alkali-metal-free bent-sandwich lanthanide amido complexes with a Et_8-calix[4]-pyrrolyl ligand, and the first application of calix[4]-pyrrolyl-supported lanthanide amides as catalysts for hydrophosphonylation of aldehydes and unactivated ketones.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Lanthanide Amido Complexes Supported by a Calix[4]-pyrrolyl Ligand. The lanthanide amido complexes **2**–**4** bearing an Et_8-calix[4]-pyrrolyl ligand were synthesized through the simple silylamine elimination reaction, as depicted in Scheme 1. The reactions of the calix[4]-pyrrole $[Et_2C(C_4H_2NH)]_4$ (**1**) with 2 equiv of $[(Me_3Si)_2N]_3Ln(\mu\text{-Cl})Li(THF)_3$ in toluene at 110 °C afforded the alkali-metal-free bent-sandwich lanthanide amido bridged lanthanide amido complexes $(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-Et}_8\text{-calix[4]-pyrrolyl})\{LnN(SiMe_3)_2\}_2$ (Ln = Nd (**2**), Sm (**3**), Gd (**4**)) (Scheme 1). The complexes are sensitive to air and moisture, and they have a good solubility in either polar solvents or nonpolar solvents. The complexes were fully characterized by elemental, spectroscopic, and single-crystal X-ray analyses.

Scheme 1. Preparation of the Lanthanide Amido Complexes 2–4



X-ray analyses reveal that complexes **2**–**4** are isostructural centrosymmetric dinuclear structures, and a representative structure diagram is shown in Figure 1. The selected bond lengths and angles are listed in Table 1. The characteristic feature of structures in these complexes is that the bent-sandwich lanthanide amides formed a bridge, similar to *ansa*-cyclopentadienyl ligand supported lanthanide amides with respect to each metal center. The calix[4]-pyrrolyl tetra-anions

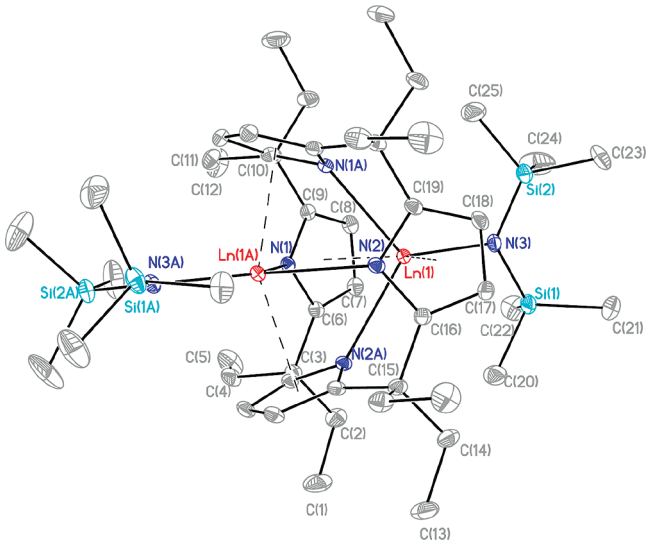


Figure 1. Representative structure of the lanthanide amido complexes containing an Et_8-calix[4]-pyrrolyl ligand. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of Complexes 2–4

	2 (Ln = Nd)	**3** (Ln = Sm)	**4** (Ln = Gd)
Ln(1)–N(1)	2.768(2)	2.737(2)	2.712(3)
Ln(1)–N(2)	2.767(3)	2.738(3)	2.708(3)
Ln(1)–N(3)	2.311(3)	2.291(3)	2.266(3)
Ln(1)–N(1A)	2.680(2)	2.659(3)	2.634(3)
Ln(1)–N(2A)	2.695(2)	2.676(2)	2.653(3)
Ln(1)–C(6)	2.895(3)	2.870(3)	2.861(3)
Ln(1)–C(7)	2.984(3)	2.969(3)	2.970(3)
Ln(1)–C(8)	2.973(3)	2.957(3)	2.955(4)
Ln(1)–C(9)	2.880(3)	2.854(3)	2.843(3)
Ln(1)–C(16)	2.881(3)	2.867(3)	2.845(3)
Ln(1)–C(17)	2.967(3)	2.946(3)	2.941(4)
Ln(1)–C(18)	2.960(3)	2.940(3)	2.933(3)
Ln(1)–C(19)	2.877(3)	2.858(3)	2.836(3)
N(1A)–Ln(1)–N(2A)	103.45(8)	103.35(8)	103.73(8)
N(3)–Ln(1)–Ln(1A)	178.44(8)	178.36(8)	178.16(8)

are bonded to the lanthanide ion in $\eta^5{:}\eta^1{:}\eta^5{:}\eta^1$-binding modes. Each lanthanide ion adopts a distorted trigonal-bipyramidal geometry with a $N(SiMe_3)_2$ and four pyrrolyls, in which two opposite pyrrole rings coordinate to one lanthanide ion in η^5 modes, and the nitrogen atoms of other two pyrrolyl rings bond to another lanthanide ion in η^1 modes.

The average distance between lanthanide ions with the five-membered pyrrolyl ring of 2.895(3) Å in complex **2** is slightly longer than the corresponding values of 2.874(3) and 2.860(4) Å found in **3** and **4**, respectively, due to reflection of lanthanide contraction from Nd^{3+} to Sm^{3+} to Gd^{3+}. The average distance between neodymium ions and the five-membered pyrrolyl ring of 2.895(3) Å in complex **2** is compared with those of 2.895(3) Å in $(\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-Me}_8\text{-calix[4]-pyrrole})\{DyN(SiMe_3)_2\}_2$[5] and 2.898(3) Å in $\{\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}(CH_2)_5C(C_4H_2N)\}_4\{NdN(SiMe_3)_2\}_2$.[5] The bond distances between samarium ions and the five-membered pyrrolyl ring ranging from 2.737(3) to 2.969(3) Å in complex **2** is comparable to the corresponding values in ate samarium complexes $(Et_8\text{-calix[4]-pyrrole})Sm_2\{(\mu\text{-Cl})_2[Li(THF)_2]\}_2$ [2.860(3)–2.967(3) Å][3b] and

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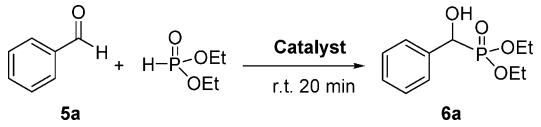
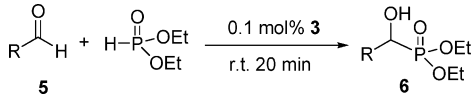
Table 2. Optimizations of Hydrophosphonylation of Benzaldehyde Catalyzed by the Lanthanide Amido Complexes[a]



entry	cat. (mol %)	solvent	yield (%)[b]
1	**3** (0.1 mol %)	THF	98
2	**3** (0.1 mol %)	toluene	92
3	**3** (0.1 mol %)	Et_2O	95
4	**3** (0.1 mol %)	*n*-hexane	94
5	**3** (0.1 mol %)	CH_2Cl_2	66
6	**3** (0.1 mol %)	solvent-free	81
7	**3** (0.05 mol %)	THF	39
8	**2** (0.1 mol %)	THF	97
9	**4** (0.1 mol %)	THF	98

[a]Reaction conditions: benzaldehyde (10.0 mmol), diethyl phosphite (12.0 mmol), solvent (2 mL), room temperature. [b]Isolated yields.

Table 3. Hydrophosphonylation of Aldehydes Catalyzed by the Catalyst 3[a]



entry	R	product	yield (%)[b]
1	Ph	**6a**	98
2	4-MePh	**6b**	99
3	2-MeOPh	**6c**	92
4	3-MeOPh	**6d**	98
5	4-MeOPh	**6e**	98
6	4-BrPh	**6f**	93
7	3-ClPh	**6g**	93
8	4-ClPh	**6h**	94
9	2,4-Cl_2Ph	**6i**	94
10	2-O_2NPh	**6j**	97
11	3-F_3CPh	**6k**	88
12	pyridin-2-yl	**6l**	83
13	pyridin-3-yl	**6m**	98
14	thiophen-2-yl	**6n**	71
15	thiophen-3-yl	**6o**	94
16	furan-2-yl	**6p**	94
17	*n*-Pr	**6q**	95
18	*i*-Pr	**6r**	93
19	*n*-Bu	**6s**	95
20	$CH_3(CH_2)_4$	**6t**	92

[a]Reaction conditions: aldehyde (10.0 mmol), diethyl phosphite (12.0 mmol), catalyst (0.1 mol %), solvent: THF (2 mL), room temperature. [b]Isolated yields.

(Et_8-calix[4]-pyrrole)$Sm_2\{(\mu\text{-}CH_3)_2[Li(THF)_2]\}_2$ [2.885(4)−2.974(4) Å].[3b] The average distance between samarium ions and the five-membered pyrrolyl ring of 2.874(3) Å in **3** is slightly shorter than the corresponding values of 2.905(3) Å in *N*-methylpyrrolyl samarium amido complexes in which the samarium ion is coordinated by the neutral *N*-methylpyrrole units in η^5 modes.[13] The σ-bonded Ln−N distances in complexes **2**−**4**, ranging from 2.266(5) to 2.311(3) Å, are obviously shorter than the η^5- and η^1-bonded Ln−N distances of 2.634(3)−2.768(3) Å in complexes **2**−**4**, respectively. The σ-bonded Ln−N distance of 2.291(3) Å in complex **3** is comparable to the corresponding values of 2.265(3) Å in $\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1$-2-$[(2,4,6\text{-}Me_3C_6H_2)NCH_2]C_4H_3N]SmN(SiMe_3)_2\}_2$[17] and 2.264(4) Å in (EBI)$SmN(SiMe_3)_2$.[18] The angles of two lanthanide ions and nitrogens of $N(SiMe_3)_2$ ranging from 178.16° to 178.44° indicated that the two central metal ions and two nitrogen atoms of $N(SiMe_3)_2$ are almost in the linear form.

Addition of Diethyl Phosphite to Aldehydes Catalyzed by the Lanthanide Amido Complexes Containing a Calix[4]-pyrrolyl Ligand. The addition reaction of diethyl phosphite with benzaldehyde was first investigated in the presence of the lanthanide amido complexes **2**−**4**, and the results are summarized in Table 2. After optimizing the reaction conditions, we were pleased to find that the reaction of diethyl phosphite to benzaldehyde all gave the corresponding product **6a** in high yields (≥92%) in the presence of 0.1 mol % of the samarium amide in the different solvents except for CH_2Cl_2 (Table 2, entries 1−5), indicating the solvents' effects on the reaction. However, the product yield could be decreased from

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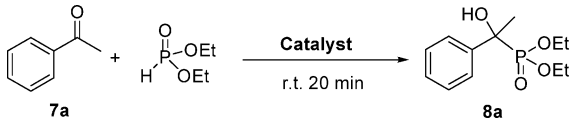
Table 4. Optimizations of Catalytical Hydrophosphonylation of Acetophenone[a]



7a 8a

entry	cat (mol %)	solvent	yield (%)[b]
1	**2** (1%)	THF	91
2	**2** (0.5%)	THF	91
3	**2** (0.2%)	THF	91
4	**2** (0.1%)	THF	91
5	**2** (0.05%)	THF	39
6	**2** (0.05%)	toluene	42
7	**2** (0.1%)	toluene	90
8	**2** (0.1%)	*n*-hexane	88
9	**2** (0.1%)	Et_2O	91
10	**3** (0.1%)	THF	89
11	**4** (0.1%)	THF	91
12	$[(Me_3Si)_2N]_3Sm(\mu\text{-Cl})Li(THF)_3$ (0.1%)	THF	<5
13	$[(Me_3Si)_2N]_3Sm(\mu\text{-Cl})Li(THF)_3$ (1%)	THF	70

[a]Reaction conditions: acetophenone (10.0 mmol), phosphite (12.0 mmol), solvent (2 mL), room temperature. [b]Isolated yields.

98% to 39% by lowering the catalytic loading from 0.1 to 0.05 mol % (Table 2, entry 7). It should be noted that the Ln^{III} ionic radii in the complexes had little effect on the catalytic activity on the hydrophosphonylation of benzaldehyde, and all of complexes gave the product **6a** in excellent yields (Table 2, entries 8 and 9).

Under the optimized reaction conditions, we next examined the substrate scope of the hydrophosphonylation reaction in the presence of the samarium amide **3** (0.1 mol %) in THF (Table 3). The results showed that the addition of diethyl phosphite to a variety of aromatic aldehydes afforded the corresponding α-hydroxy phosphonates in excellent yields of ≥88%, regardless of the electronic nature or the steric effects of the substituents on the aryl groups (Table 3, entries 1−9). Heteroaromatic aldehydes, such as pyridine-2-carboxaldehyde, pyridine-3-carboxaldehyde, thiophene-2-carboxaldehyde, thiophene-3-carboxaldehyde, and 2-furaldehyde, also worked well, and the α-hydroxy phosphonates **6j**−**6n** were obtained in good to excellent yields (Table 3, entries 10−14). Interestingly, both linear and branched aliphatic aldehydes were also efficiently used as the substrates in the presence of the catalyst **3** to afford the corresponding α-hydroxy phosphonates in high yields (Table 3, entries 15−18).

Addition of Diethyl Phosphite to Ketones Catalyzed by the Lanthanide Amido Complexes Containing a Calix[4]-pyrrolyl Ligand. To further investigate the scope of the application for the hydrophosphonylation reaction, we paid attention to a more challenging system, that is, the lanthanide amide catalyzed reaction of unactivated ketones with dialkyl phosphate. To obtain the good result, various reaction conditions for the addition of diethyl phosphite to acetophenone were examined in the presence of calix[4]-pyrrolyl lanthanide amido complexes, and the results are summarized in Table 4. The reaction of diethyl phosphite with acetophenone in the presence of 1−0.1 mol % of the neodymium amide **2** was carried out, respectively. To our delight, in all cases, the desired product **8** was obtained in high yields (up to 91%) (Table 4, entries 1−4). While the catalyst loading was reduced from 0.1 to 0.05 mol %, the yields of the product decreased dramatically from 91% to 39% (Table 4, entries 5 and 6). Next, investigations for the choice of the solvent indicated that the catalyst was compatible with a variety of solvents, such as toluene, *n*-hexane, and diethyl ether, and high yields of the product (>88% yield, Table 4, entries 4, 7−9) were obtained using the neodymium amide **2** as a catalyst, indicating the solvent compatibility of the catalyst. Therefore, we selected a catalyst loading of 0.1 mol % in THF for the following reactions. Examination of the catalytic activity of the different lanthanide amides on hydrophosphonylation of ketones also showed that high yields of product were obtained in the presence of different catalysts, indicating that the ionic radii of the lanthanide metals have little influence on the catalytic activity on the hydrophosphonylation of acetophenone. Notably, a control experiment revealed that $[(Me_3Si)_2N]_3Sm(\mu\text{-Cl})Li(THF)_3$ as the catalyst displayed poor catalytic activity under the same reaction conditions (Table 4, entries 12 and 13), suggesting the ligands' and bimetal center's effect on the catalytic activity for hydrophosphonylation of acetophenone.

The substrate scope of catalytic hydrophosphonylation of unactivated ketones was then investigated using the neodymium amide **2** as a catalyst in THF at room temperature, and the results are presented in Table 5. We found that the electronic nature of the substituents on the aryl groups had some effect on the reactivity of hydrophosphonylation of ketones. When the substituents on the phenyl ring are the electron-withdrawing ones, such as O_2N−, Cl−, Br−, F−, F_3C−, and Ph−, the products **8b**−**8j** can be isolated in good to high yields (Table 5, entries 2−10). While the substituents on the phenyl ring are the electron-donating groups, such as CH_3O− and CH_3−, moderate yields of the compounds **8k**−**8m** (Table 5, entries 11−13) were achieved after 2 h. It was also found that the steric hindrance of the substrates had an significant effect on the reactivity of the hydrophosphonylation of ketones; for example, the addition of diethyl phosphite to 4′-bromoacetophenone gave the product **8g** in 95% yield for only 20 min (Table 5, entry 7), whereas the addition of diethyl phosphite to 2′-bromoacetophenone gave the product in only 79% yield even in 2 h (Table 5, entry 6). Similarly, 4′-methylacetophenone was converted to the corresponding product **8l** in 76% yield (Table 5, entry 12), whereas 2′-methylacetophenone gave the product **8k** in only 41% yield

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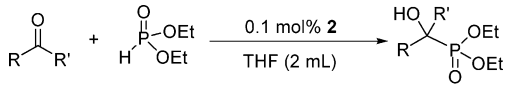
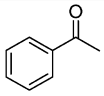
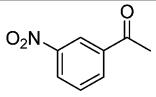
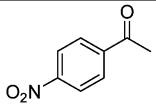
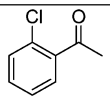
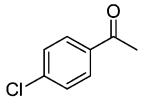
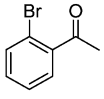
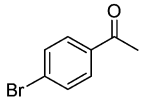
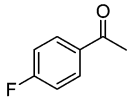
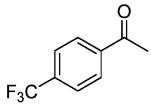
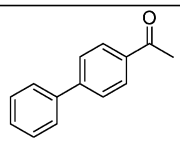
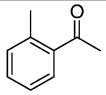
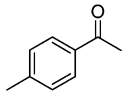
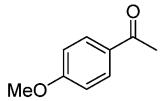
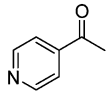
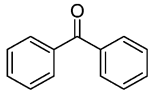
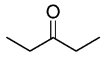
Table 5. Hydrophosphonylation of Ketones Catalyzed by the Calix[4]-pyrrolyl Amido Neodymium Complex[a,b]



7 8

Entry	Ketones	Time (min)	Product	Yield(%)[b]
1		20	**8a**	91
2		20	**8b**	94
3		20	**8c**	97
4		20	**8d**	86
5		20	**8e**	94
6		120	**8f**	79
7		20	**8g**	95
8		20	**8h**	93
9		20	**8i**	97
10		20	**8j**	90
11		120	**8k**	41
12		120	**8l**	76
13		120	**8m**	63
14		20	**8n**	93
15		20	**8o**	92
16		20	**8p**	93
17		20	**8q**	92
18		20	**8r**	94
19		20	**8s**	90

[a]Reaction conditions: ketone (10.0 mmol), phosphite (12.0 mmol), catalyst **2** (0.1 mol %), THF (2 mL), room temperature. [b]Isolated yields.

after 2 h (Table 5, entry 11). A heteroaromatic ketone, such as 4-acetylpyridine, was also efficiently used as the substrate under the optimal reaction conditions to form the α-hydroxy phosphonate **8n** in an excellent yield (Table 5, entry 14). Interestingly, an excellent yield of **8o** was achieved when benzophenone was treated with diethyl phosphate employing the neodymium amide **2** as a catalyst (Table 5, entry 15). It should be noted that the catalyst **2** also worked well for both linear and branched aliphatic ketones, affording the corresponding α-hydroxy phosphonates in high yields (Table 3, entries 16 and 17). Furthermore, nonmethyl ketones, such as 3-pentanone and cyclohexanone, were also applicable to this reaction, and the reaction afforded corresponding α-hydroxy phosphonates **8r** and **8s** in 94% and 90% yields, respectively (Table 3, entries 18 and 19).

CONCLUSIONS

In summary, the dinuclear trivalent lanthanide amido complexes bearing a tetra-anion calix[4]-pyrrolyl ligand were synthesized by the simple silylamine elimination reaction of calix[4]-pyrrole with the lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$. The X-ray diffraction analyses discovered that the key features of the structures of these complexes were that the bent-sandwich lanthanide amido formed a bridge, similar to *ansa*-cyclopentadienyl ligand supported lanthanide amides with respect to each metal center and that the two pyrrolyl rings in each metal center took the eclipsed form. All of these lanthanide amido complexes displayed high catalytic activities for hydrophosphonylation of aldehydes and unactivated ketones. The addition of diethyl phosphite to aldehydes and ketones afforded the products in high yields of up to 97% by

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employing low loadings of the catalysts (0.1 mol %) at room temperature in a very short time (20 min). The catalysts are suitable for a series of organic solvents and work well for a wide range of aliphatic, aromatic, and heteroaromatic aldehydes and ketones. The results highlight the first application of calix[4]-pyrrolyl-supported lanthanide amides as catalysts for hydrophosphonylation of unactivated ketones. Further investigations of new catalytic systems for hydrophosphonylation of unactivated ketones are in progress.

EXPERIMENTAL SECTION

General Remarks. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and a oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. Solid aldehydes and ketones were directly used, and liquid aldehydes and ketones were distilled before use. $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$[19] and $[Et_2C(C_4H_2NH)]_4$[20] were prepared according to literature methods. IR spectra were recorded on a SHIMADZU FTIR-8400S spectrometer. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a Bruker AV-300 NMR spectrometer in $CDCl_3$. The chemical shifts are reported in parts per million relative to the internal standard TMS (^{1}H NMR), to residual signals of the solvents ($CHCl_3$, 77.0 ppm for ^{13}C NMR) and to the external standard 85% H_3PO_4 (^{31}P NMR).

Synthesis of (η^5:η^1:η^5:η^1-Et$_8$-Calix[4]-pyrrole){NdN(SiMe$_3$)$_2$}$_2$ (2). To a toluene (30.0 mL) solution of $[(Me_3Si)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3$ (0.958 g, 1.08 mol) was added a toluene (10.0 mL) solution of ligand **1** (0.293 g, 0.54 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was stirred at 110 °C for 24 h. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2 × 10.0 mL). The extractions were combined and concentrated to about 10.0 mL. Pale blue crystals were obtained by recrystallization from the concentrated *n*-hexane solution at 0 °C (0.327 g, 57% yield). mp 263 °C. IR (KBr pellets): ν 3437 (s), 2963 (s), 2934 (s), 2874 (m), 1574 (m), 1501 (m), 1458 (m), 1414 (m), 1379 (m), 1331 (w), 1281 (w), 1198 (m), 1182 (m), 1051 (m), 932 (m), 841(m), 762 (s) cm^{-1}. Anal. Calcd for $C_{48}H_{84}N_6Si_4Nd_2$: C, 50.30; H, 7.39; N, 7.33. Found: C, 49.88; H, 7.23; N, 7.02.

Synthesis of (η^5:η^1:η^5:η^1-Et$_8$-Calix[4]-pyrrole){SmN(SiMe$_3$)$_2$}$_2$ (3). Complex **3** was prepared as yellow crystals in 52% yield from the reaction of compound **1** (0.277 g, 0.51 mmol) with $[(Me_3Si)_2N]_3Sm(\mu\text{-}Cl)Li(THF)_3$ (0.912 g, 1.02 mol) by employing the procedures similar to those used for the preparation of **2**. mp 259 °C. IR (KBr pellets): ν 3437 (s), 2965 (s), 2931 (s), 2876 (m), 1574 (m), 1500 (m), 1461 (m), 1414 (m), 1379 (m), 1332 (m), 1280 (w), 1198 (m), 1182 (m), 1051 (m), 933 (m), 841 (m), 763 (s) cm^{-1}. Anal. Calcd for $C_{48}H_{84}N_6Si_4Sm_2$: C, 49.77; H, 7.31; N, 7.26. Found: C, 49.62; H, 7.07; N, 7.14.

Synthesis of (η^5:η^1:η^5:η^1-Et$_8$-Calix[4]-pyrrole){GdN(SiMe$_3$)$_2$}$_2$ (4). Complex **4** was prepared as colorless crystals in 53% yield from the reaction of compound **1** (0.283 g, 0.52 mmol) with $[(Me_3Si)_2N]_3Gd(\mu\text{-}Cl)Li(THF)_3$ (0.933 g, 1.04 mol) by employing the procedures similar to those used for preparation of **2**. mp 261 °C. IR (KBr pellets): ν 3437 (s), 2965 (s), 2932 (s), 2873 (m), 1574 (m), 1500 (m), 1458 (m), 1414 (m), 1377 (m), 1331 (m), 1281 (w), 1252(m), 1198 (m), 1099 (w), 1051 (m), 926 (m), 841 (m), 762 (s),706 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{68}N_6Si_4Gd_2$: C, 49.19; H, 7.22; N, 7.17. Found: C, 49.42; H, 7.08; N, 6.98.

Crystal Structure Determinations. Suitable crystal of complexes **2**–**4** was each mounted in a sealed capillary. Diffraction was performed on a Burker SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[21] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[22] All hydrogen atoms were refined using a riding model. See Table6 for crystallographic data.

Table 6. Crystallographic Data for the Complexes 2–4

	2	3	4
formula	$C_{48}H_{84}Nd_2N_6Si_4$	$C_{48}H_{84}Sm_2N_6Si_4$	$C_{48}H_{84}Gd_2N_6Si_4$
formula wt	1146.05	1158.27	1172.07
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/c	*C*2/c	*C*2/c
a (Å)	18.6562(12)	18.6547(11)	18.6298(14)
b (Å)	14.4656(9)	14.4585(8)	14.4462(11)
c (Å)	21.5024(14)	21.4286(12)	21.3833(16)
β (deg)	104.4540(10)	104.2550(10)	104.0420(10)
V (Å^3)	5619.2(6)	5601.7(6)	5582.9(7)
T (K)	293(2)	293(2)	293(2)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.355	1.373	1.394
μ (mm^{-1})	1.948	2.197	2.476
F(000)	2360	2376	2392
θ range (deg)	1.80–27.58	1.80–27.56	1.80–27.64
reflns collected	23 988	23 979	23 561
unique reflns	6454 (R_{int} = 0.0221)	6450 (R_{int} = 0.0261)	6493 (R_{int} = 0.0258)
parameters	282	282	282
goodness of fit	1.151	1.026	1.100
R_1 ($I > 2\sigma(I)$)	0.0281	0.0274	0.0285
wR_2 ($I > 2\sigma(I)$)	0.0717	0.0667	0.0714
largest diff. peak and hole (e·Å^{-3})	0.984 and −0.857	0.800 and −0.614	0.860 and −0.952

General Procedures for Hydrophosphonylation of Aldehydes. A 30.0 mL Schlenk tube under dried argon was charged with the calix[4]-pyrrolyl lanthanide amido complex **3** (11.6 mg, 0.01 mmol), diethyl phosphite (1.66 g, 12 mmol), and THF (2.0 mL); then aldehyde (10.0 mmol) was added to the mixture. The resulting mixture was allowed to stir at room temperature for 20 min. After the reaction was completed, the reaction mixture was hydrolyzed by water (3.0 mL), extracted with ethyl acetate (3 × 10.0 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under the reduced pressure, the final products were further purified by washing with hexane. The characterization data for the resulting products can be read in the Supporting Information.

General Procedures for Hydrophosphonylation of Ketones. A 30.0 mL Schlenk tube under dried argon was charged with the calix[4]-pyrrolyl lanthanide amido complex **2** (11.5 mg, 0.01 mmol), diethyl phosphite (1.66 g, 12 mmol), and THF (2.0 mL); then ketone (10.0 mmol) was added to the mixture. The resulting mixture was allowed to stir at room temperature for 20 min. After the reaction was completed, the reaction mixture was hydrolyzed by water (3.0 mL), extracted with ethyl acetate (3 × 10.0 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under the reduced pressure, the final products were further purified by washing with hexane. The characterization data for the resulting products can be read in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The characterization data for α-hydroxy phosphonates and X-ray crystallographic files, in CIF format, for structure determination of complexes **2**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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