



Synthesis and characterization of amidate rare-earth metal amides and their catalytic activities toward hydrophosphonylation of aldehydes and unactivated ketones



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ABSTRACT

Two novel amidate rare-earth metal amides $\text{Ln}[\text{N}(\text{SiMe}_3)_2](\kappa^2\text{-L}^1)_2(\text{THF})$ ($\text{L}^1 = \text{C}_6\text{H}_5\text{C}(\text{O})\text{NC}_6\text{H}_3(\text{iPr})_2$) ($\text{Ln} = \text{Yb}$ (**1**), Y (**2**)) were prepared through simple silylamine elimination reactions of the benzamide proligand HL^1 with $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ in tetrahydrofuran at 60 °C. These complexes were well characterized by elemental and single-crystal X-ray diffraction analyses, and the yttrium complex **2** was also characterized by NMR spectroscopic analyses. Investigation on the catalytic behaviors of amidate rare-earth metal amides, including two new complexes **1**, **2** and three known amidate divalent rare-earth metal amides $\{\text{Ln}[\text{N}(\text{SiMe}_3)_2](\mu\text{-O}:\kappa^2\text{-L}^1)(\text{THF})\}_2$ ($\text{Ln} = \text{Yb}$ (**3**), Eu (**4**)), and $\text{Eu}_2[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-O}:\kappa^2\text{-L}^2)_2(\text{THF})_3$ ($\text{L}^2 = \text{C}_6\text{H}_5\text{-C}(\text{O})\text{NC}_6\text{H}_3(\text{Me})_2$) (**5**), revealed that all complexes exhibited high catalytic activities toward the hydrophosphonylation of aldehydes and some of them showed moderate to good activities toward unactivated ketones. Complex **1** showed the highest activity, which afforded a series of α -hydroxy phosphonates in good to excellent yields at room temperature after short time with low catalyst loadings.

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1. Introduction

Since many biologically active compounds used as antiviral, antitumoral agents, enzyme inhibitors, HIV protease, and polymerase have the structural unit of α -hydroxy phosphonates, the synthesis of α -hydroxy phosphonates has received growing attention in the past four decades [1]. Diverse starting materials were employed to achieve the synthetic goal [2]. Undoubtedly, the most straightforward and atom-economic pathway for C–P bond formation, especially for the synthesis of α -hydroxy phosphonates, is the addition of dialkyl phosphites to carbonyl compounds which is now known as the Pudovik reaction [3]. Early in 1960, Bengelsdorf found that this reaction took place under thermal noncatalyzed conditions [4]. However, the substrate scope was limited, and the yields of the target molecules were poor even after long-time reaction at relatively high temperature. Until the end of 1970s, Pudovik announced the convenient preparation of α -hydroxy phosphonates in the presence of diethylamine or a catalytic amount of sodium alkoxide [3a]. In the ensuing 40 years, various catalysts have been explored to promote this transformation, such as mineral salts (e.g., Al_2O_3 [5], CaO [6], KF [7] and MoO_2Cl_2 [8]), Lewis acids (e.g., TiCl_4 [9] and $\text{Ti}(\text{O}^i\text{Pr})_4$ [10]), Lewis bases (e.g., Et_3N [11], pyridine

[12], tetramethylguanidine (TMG) [13], 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-methyl derivative of TBD (MTBD) and polymer-supported-TBD (P-TBD) [14]), Brønsted bases (e.g., RONa [15]) and some organic molecules (e.g., cinchona alkaloids [16] and cinchona-derived thiourea [17]). All these meaningful results powerfully showed the growing importance of the Pudovik reaction in both scientific research and commercial process. However, these systems still have some disadvantages. For example, some systems require relatively high catalyst loading (more than 10 mol%) [6,7b,9,10a–b,17] and long reaction time [6,7b,8,9,10b,13,17]. In other cases, α -hydroxy phosphonates are easily cleaved to regenerate the starting carbonyl compounds in alkaline medium [4,18]. Recently, various metal complexes, including aluminum [19], titanium [20], niobium [21], alkaline earth metal [22] and rare-earth metal complexes [23] have been proved to be effective catalysts for the hydrophosphonylation of aldehydes under mild conditions. However, their activities are in general limited in the hydrophosphonylation of unactivated ketones. Tridentate Schiff-base- Et_2AlCl complexes [24], rare-earth metal amido complexes [23g,h,j], and lanthanide anilido complexes [23i], developed by Feng's, Wang's and Yao's groups, respectively, deserve special mention, owing to their excellent catalytic activities (yields up to 99%) for the hydrophosphonylation of both aldehydes and unactivated ketones. Hence, in the long term, the development of new catalytic systems is still highly desirable.

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Amidates have been identified as a family of easily prepared and highly variable [N, O] ligands, which can adopt a variety of coordination modes in lanthanide chemistry [25]. Moreover, the steric environment and electronic properties of amidate ligands can be finely tuned by changing acyl groups or substituents on the nitrogen atom. Hence, many researchers put their emphasis on amidate ligands. A lot of transition metal and rare-earth metal amidate complexes have emerged and showed not only great applications in catalytic transformations, such as hydroamination and hydroamination/cyclization of alkenes [26], alkynes [27] and allenes [28], allylic etherification [29], olefin oxidation [30], three-component Strecker reaction [31], Heck-type reaction [32], amidation of aldehydes [33], and the addition of terminal alkynes to nitriles [34], but also high activities in ring-opening polymerization of lactones [25,26,35], oligomerization and polymerization of ethylene [36], and insertion reactions [37].

In the course of our effort to further develop the application of rare-earth metal amidate complexes, two novel benzamide rare-earth metal amides $\text{Ln}[\text{N}(\text{SiMe}_3)_2](\kappa^2\text{-L}^1)(\text{THF})$ ($\text{Ln} = \text{Yb}$ (**1**), Y (**2**)) were successfully prepared via simple metathesis reactions of benzamide HL^1 and rare-earth metal precursors $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{Ln} = \text{Yb}$, Y). For the first time, the catalytic activities of amidate complexes **1** and **2** on the hydrophosphonylation of both aldehydes and unactivated ketones have been studied. In addition, they were compared with three known divalent rare-earth metal amides **3–5** bearing the same or different amidate ligands. The influence of the central metals and their oxidation states on the catalytic behavior are reported here.

2. Experimental

2.1. General procedures

All manipulations and reactions were conducted under purified argon and oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. Rare-earth metal precursors $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{Ln} = \text{Yb}$, Y) [38a], $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{Ln} = \text{Yb}$, Eu) [38b,c], and proligand *N*-(2,6-diisopropylphenyl)benzamide and *N*-(2,6-dimethylphenyl)benzamide [39] were prepared according to literature methods. All solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. Solid aldehydes and ketones were degassed before use, and liquid aldehydes and ketones were distilled from CaH_2 or molecular sieve prior to use. The single crystal X-ray diffraction data were recorded on a Rigaku Mercury CCD X-ray diffractometer. ^1H , ^{13}C and ^{31}P NMR spectra were obtained on a Unity Inova-400 spectrometer in C_6D_6 or CDCl_3 . Chemical shifts (δ) were internally referred to signals of tetramethylsilane (TMS) (^1H and ^{13}C) or externally to 85% H_3PO_4 (^{31}P), and are reported in ppm. Metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. Melting points were determined in sealed Ar-filled capillary tubes and are uncorrected.

2.2. Synthesis of $\text{Yb}[\text{N}(\text{SiMe}_3)_2](\kappa^2\text{-L}^1)(\text{THF})\cdot\text{C}_7\text{H}_8$ (**1**· C_7H_8)

To a stirred tetrahydrofuran solution of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_3$ (2.00 mmol, 20 mL of THF), *N*-(2,6-diisopropylphenyl)benzamide (1.12 g, 4.00 mmol) in 20 mL THF was slowly added. The mixture was stirred at 60 °C for 15 h. After that, the solvent was pumped off, and the residue was recrystallized from toluene at room temperature to give **1** as pale yellow crystals. Yield: 1.36 g (67%). Mp. 129.6–131.2 °C. *Anal.* Calc. for $\text{C}_{55}\text{H}_{78}\text{N}_3\text{O}_3\text{Si}_2\text{Yb}$ (1058.42): C, 62.36; H, 7.37; N, 3.97; Y, 16.35. Found: C, 61.97; H, 7.25; N, 4.17; Y, 16.57%.

2.3. Synthesis of $\text{Y}[\text{N}(\text{SiMe}_3)_2](\kappa^2\text{-L}^1)(\text{THF})\cdot 0.5\text{C}_7\text{H}_8$ (**2**· $0.5\text{C}_7\text{H}_8$)

Following the method described for complex **1**, reaction of *N*-(2,6-diisopropylphenyl)benzamide (1.12 g, 4.00 mmol) and $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (2.00 mmol, 20 mL of tetrahydrofuran) afforded colorless crystals **2** in toluene. Yield: 1.37 g (74%). Mp. 132.9–134.5 °C. *Anal.* Calc. for $\text{C}_{51.5}\text{H}_{74}\text{N}_3\text{O}_3\text{Si}_2\text{Y}$ (928.23): C, 66.58; H, 7.97; N, 4.52; Y, 9.58. Found: C, 66.17; H, 7.91; N, 4.47; Y, 9.63%. ^1H NMR (400 MHz, C_6D_6): δ 7.72 (d, $J = 1.36$ Hz, 1H, phenyl H), 7.70 (d, $J = 1.84$ Hz, 1H, phenyl H), 7.60 (d, $J = 1.32$ Hz, 3H, phenyl H), 7.58 (d, $J = 1.76$ Hz, 3H, phenyl H), 7.14 (m, 3H, phenyl H), 7.10 (s, 10H, phenyl H), 7.06–7.01 (m, 4H, phenyl H), 6.91–6.84 (m, 12H, phenyl H), 3.95 (m, 8H, OCH_2), 3.56 (heptet, $J = 6.84$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 2.11 (s, 3H, CH_3), 1.25 (d, $J = 6.60$ Hz, 18H, $\text{CH}(\text{CH}_3)_2$), 1.16 (d, $J = 6.76$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$ and 8H, CH_2 of THF), 0.96 (d, $J = 6.84$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.91 (d, $J = 6.44$ Hz, 18H, $\text{CH}(\text{CH}_3)_2$), 0.51 (s, 30H, $\text{Si}(\text{CH}_3)_3$), 0.10 (s, 6H, $\text{Si}(\text{CH}_3)_3$) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ 177.26, 142.97, 141.65, 141.41, 134.29, 131.00, 130.49, 130.35, 129.33, 128.57, 125.70, 125.51, 124.33, 124.15, 70.09, 28.54, 25.10, 24.92, 24.28, 5.23, 2.65 ppm.

2.4. Synthesis of $\{\text{Yb}[\text{N}(\text{SiMe}_3)_2](\mu\text{-O}:\kappa^2\text{-L}^1)(\text{THF})\}_2$ (**3**) [34]

To a stirred tetrahydrofuran solution of $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ (2.00 mmol, 20 mL of THF), *N*-(2,6-diisopropylphenyl)benzamide (0.56 g, 2.00 mmol) in 20 mL THF was slowly added. The mixture was stirred at 60 °C for 4 h. After that, the solvent was pumped off, and the residue was recrystallized from a mixture solution of THF and *n*-hexane at room temperature to give **3** as black crystals.

2.5. Synthesis of $\{\text{Eu}[\text{N}(\text{SiMe}_3)_2](\mu\text{-O}:\kappa^2\text{-L}^1)(\text{THF})\}_2$ (**4**) [34]

Following the method described for complex **3**, reaction of *N*-(2,6-diisopropylphenyl)benzamide (0.56 g, 2.00 mmol) and $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ (2.00 mmol, 20 mL of THF) afforded yellow crystals **4** in a mixture solution of THF and *n*-hexane.

2.6. Synthesis of $\text{Eu}_2[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-O}:\kappa^2\text{-L}^2)(\text{THF})_3$ (**5**) [34]

Following the method described for complex **3**, reaction of *N*-(2,6-dimethylphenyl)benzamide (0.45 g, 2.00 mmol) and $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})_2$ (2.00 mmol, 20 mL of THF), afforded yellow crystals **5** in a mixture solution of THF and *n*-hexane.

2.7. X-ray structure determination of complexes **1** and **2**

Owing to their air and moisture sensitivity, suitable single crystals of complexes **1** and **2** were each sealed in thin-walled glass capillaries. Intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromatized $\text{Mo K}\alpha$ ($\lambda = 0.71075$ Å) radiation for complex **2**, and $\text{Cu K}\alpha$ ($\lambda = 1.54184$ Å) radiation for complex **1**. Details of the intensity data collection and crystal data are given in Tables 1 and 2. The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by fullmatrix least-squares analysis on F^2 . All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. The structures were solved and refined by using the SHELXL-97 program [40].

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