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Synthesis and characterization of ytterbium guanidinates stabilized by bridged bis(phenolate) ligand and their application for the hydrophosphonylation reaction of aldehydes

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ABSTRACT

A series of ytterbium guanidinato complexes stabilized by an amine-bridged bis(phenolate) ligand were prepared, and their catalytic property for the hydrophosphonylation reaction of aldehydes was explored. Metathesis reactions of amine-bridged bis(phenolate) ytterbium chlorides LYbCl(THF) [L = $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2^tBu_2\text{-}3,5)\}_2$] with corresponding lithium guanidinates in a 1:1 molar ratio in THF gave the expected ytterbium guanidinato complexes $LYb[R_2NC(NR^1)_2]$ [R^1 = Cy, $R_2N = N(TMS)_2$ (**1**), $N(CH_2)_5$ (**2**); $R^1 = {}^i$Pr, $R_2N = N(TMS)_2$ (**3**), NPh_2 (**4**)]. These ytterbium complexes were well characterized by elemental analyses, IR spectroscopy and single-crystal X-ray structure determination. The metal ion is six-coordinated by two oxygen and two nitrogen atoms from the bis(phenolate) ligand, and two nitrogen atoms from one guanidinato group. The coordination geometry around ytterbium can be described as a distorted octahedron. It was found that these ytterbium guanidinato complexes are highly efficient catalysts for the hydrophosphonylation reaction of various aldehydes under mild conditions.

Introduction

In recent years, amine bridged bis(phenol)s, as a type of dianionic ligands, have received considerable attention in organolanthanide chemistry, because these ligand systems have attractive features, such as easily available, tunable and potentially recyclable, which provides the possibility for understanding the relationship between the structure of the bis(phenolate)ligand and the catalytic property of the corresponding lanthanide complexes [1–16]. It has been found that some of bridged bis(phenolate)lanthanide complexes are efficient initiators for the ring-opening polymerization of cyclic esters, giving the polymers both in high conversions and with high molecular weights, and excellent stereoselectivity for *rac*-lactide (LA) and *rac*-β-butyrolactone (BBL) polymerization [5,7–9,15], which may be attributed to the rigid backbone of the ligand to provide fixed coordination environment around the metal center.

Recently, we became interested in studying the synthesis and catalytic behavior of organometallic complexes supported by the bulky bridged bis(phenolate) ligands [10–18]. It was found that the carbon-bridged bis(phenolate) lanthanide alkoxo complexes are efficient initiators for the controlled polymerization of ε-caprolactone [17]. The lanthanide aryloxides and alkoxides stabilized by amine bridged bis(phenolate) ligand are efficient initiators for the stereoselective controlled polymerization of *rac*-lactide and *rac*-β-butyrolactone [13,15]. Cationic amidozirconium and titanium complexes bearing an amine-bridged bis(phenolato) ligand are highly efficient catalysts for regioselective intermolecular hydroamination reactions of various terminal alkynes and anilines, with good to excellent yields and 100% Markovnikov selectivity [18]. To gain better understanding of this ligand system, development of new catalytic system involving bridged bis(phenolato) ligand is still required. In this article, several ytterbium guanidinato complexes stabilized by an amine bridged bis(phenolate) ligand were synthesized, and it was found that these ytterbium complexes are highly efficient catalysts for the hydrophosphonylation reaction of various aldehydes under mild conditions.

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Experimental section

General considerations

All the manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. All solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. Solid aldehydes were used directly, and liquid aldehydes were distilled before use. The ligand precursor LH_2 [L = $Me_2NCH_2CH_2N\{CH_2$-(2-O–C_6H_2–$^tBu_2$-3,5)$\}_2$] [19], and LYbCl(THF) [3] were prepared according to the procedures reported in the literature. Ytterbium analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer. 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 Fourier transform IR spectrometer as KBr pellets. The ^1H NMR spectra were recorded in $CDCl_3$ for organic compounds with a Unity Varian spectrometer.

Synthesis of LYb[$(TMS)_2NC(NCy)_2$] (**1**)

A Schlenk flask was charged with $HN(TMS)_2$ (TMS = $SiMe_3$, 0.6 g, 3.7 mmol), THF (20 mL), and a stirring bar. The solution was cooled to 0 °C, and *n*-BuLi (1.85 mL, 3.7 mmol, 2 M in hexane) was added by syringe. The solution was stirred for 1 h at 0 °C, and then *N*,*N*′-dicyclohexylcarbodiimide (0.76 g, 3.7 mmol) was added. The resulting solution was slowly warmed to room temperature, and stirred for 1 h, and then was added slowly to a THF solution of LYbCl(THF) (20 mL, 2.97 g, 3.7 mmol). The mixture was stirred overnight at room temperature, and the solvent was removed in a vacuum. The residue was extracted with toluene, and LiCl was removed by centrifugation. Yellow crystals were obtained from concentrated toluene solution at room temperature in a few days (2.28 g, 58%). Anal. Calcd for $C_{53}H_{94}N_5O_2Si_2Yb$ (1062.56): C, 59.91; H, 8.92; N, 6.59; Yb, 16.29. Found: C, 59.63; H, 9.09; N, 6.74; Yb, 16.19. IR (KBr pellet, cm^{-1}): 2950 (s), 2860 (s), 2360 (w), 1627 (s), 1556 (m), 1478 (s), 1446 (m), 1414 (m), 1385 (m), 1361 (m), 1329 (m), 1307 (m), 1252 (m), 1238 (m), 997 (m), 956 (m), 938 (m), 877 (m), 838 (m), 744 (m).

Synthesis of LYb[$(CH_2)_5NC(NCy)_2$] (**2**)

The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but piperidine (0.34 g, 4 mmol) was used instead of $HN(TMS)_2$. Yellow crystals were obtained from concentrated toluene solution at room temperature in a few days (2.45 g, 62%). Anal. Calcd for $C_{52}H_{86}N_5O_2Yb$ (986.31): C, 63.32; H, 8.79; N, 7.10; Yb, 17.54. Found: C, 63.10; H, 8.97; N, 7.01; Yb, 17.43. IR (KBr pellet, cm^{-1}): 2936 (s), 2848 (s), 1628 (s), 1477 (s), 1443 (s), 1416 (s), 1357 (m), 1307 (m), 1248 (m), 1229 (m), 1202 (m), 1166 (m), 1133 (m), 1114 (m), 1050 (m), 1028 (m), 993 (m), 940 (m), 912 (m), 875 (m), 838 (m), 805 (m), 779 (m), 744 (m), 528 (m), 446 (m).

Synthesis of LYb[$(TMS)_2NC(N^iPr)_2$] (**3**)

Following the procedure similar to that for the synthesis of complex **1**, Li[$(TMS)_2NC(N^iPr)_2$] (3.5 mmol), which was formed in situ by the reaction of $LiN(TMS)_2$ with *N*,*N*′-diisopropylcarbodiimide, reacted with LYbCl(THF) (2.81 g, 3.5 mmol) in THF (20 mL) to yield yellow crystals upon crystallization from concentrated toluene solution (1.89 g, 55%). Anal. Calcd for $C_{47}H_{86}N_5O_2Si_2Yb$ (982.43): C, 57.46; H, 8.82; N, 7.13; Yb, 17.61. Found: C, 57.18; H, 8.99; N, 7.28; Yb, 17.51. IR (KBr pellet, cm^{-1}): 2953 (s), 2899 (s), 2869 (s), 2362 (w), 1628 (s), 1555 (w), 1478 (s), 1414 (m), 1388 (m), 1360 (m), 1330 (m), 1309 (m), 1252 (m), 1237 (m), 1203 (m), 1166 (m), 1131 (m), 1000 (m), 939 (m), 877 (m), 834 (m), 743 (m) 527 (m).

Synthesis of LYb[$(Ph)_2NC(N^iPr)_2$] (**4**)

The synthesis of complex **4** was carried out in the same way as that described for complex **3**, but diphenylamine (0.66 g, 3.9 mmol) was used instead of $HN(TMS)_2$. Yellow crystals were obtained from concentrated toluene solution at room temperature in a few days (2.51 g, 65%). Anal. Calcd for $C_{53}H_{78}N_5O_2Yb$ (990.26): C, 64.28; H, 7.94; N, 7.07; Yb, 17.47. Found: C, 64.03; H, 8.11; N, 7.22; Yb, 17.36. IR (KBr pellet, cm^{-1}): 2959 (s), 2899 (s), 2864 (s), 2358 (m), 1655 (s), 1599 (s), 1478 (s), 1414 (m), 1360 (m), 1308 (s), 1238 (m), 1202 (m), 1167 (m), 1133 (m), 1029 (m), 876 (m), 837 (m), 752 (m), 730 (m), 694 (m), 464 (m), 445 (m).

General procedures for hydrophosphonylation reaction

A 30.0 mL Schlenk tube under dried argon was charged with the lanthanide guanidinate complex **1** (10.6 mg, 0.01 mmol), diethyl phosphite (1.66 g, 12 mmol), then an aldehyde (10.0 mmol) was added to the mixture. The resulting mixture was allowed to stir at room temperature for 5 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 reduced pressure, the final products were further purified by washing with hexane or by column chromatography.

X-ray crystallographic structure determinations

Suitable single crystals of complexes **1**–**4** were sealed in a thin-walled glass capillary for determination the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo-Kα radiation ($\lambda = 0.71070$ Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. The hydrogen atoms in these complexes were 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. The structures were solved and refined using SHELEXL-97 programs.

Results and discussion

Synthesis and characterization of ytterbium guanidinato complexes **1**–**4**

Amine bridged bis(phenolate) ytterbium chloride LYbCl(THF) can be prepared conveniently by the reaction of anhydrous $YbCl_3$ with one equivalent of LNa_2 [L = $Me_2NCH_2CH_2N\{CH_2$-(2-O–C_6H_2–$^tBu_2$-3,5)$\}_2$] in THF [3]. The corresponding amine-bridged bis(phenolate)ytterbium guanidinato complexes can be synthesized directly by general metathesis reaction. Treatment of LYbCl(THF) with 1 equivalent of lithium guanidinates, which were freshly prepared in situ by the reaction of lithium amides with carbodiimide in THF, after workup, provided the desired ytterbium guanidinato complexes as shown in Scheme 1. Complexes **1**–**4** were well characterized by elemental analysis and IR spectroscopy. Elemental analysis suggested that the complex consists of one amine bis(phenolate) ligand, one guanidinato group and one ytterbium atom. In their IR spectra, the strong absorptions in the range of 1627–1655 cm^{-1} can be attributed to the characteristic absorptions of partial C=N double-bond, which indicated the presence of π-electrons delocalization within the N–C–N linkage.