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Synthesis, reactivity and structural characterization of lanthanide hydroxides stabilized by a carbon-bridged bis(phenolate) ligand

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ABSTRACT

The synthesis of lanthanide hydroxo complexes stabilized by a carbon-bridged bis(phenolate) ligand 2,2'methylene-bis(6-*tert*-butyl-4-methylphenoxo) (MBMP²⁻) was described, and their reactivity toward phenyl isocyanate was explored. Reactions of (MBMP)Ln(C₅H₅)(THF)₂ with a molar equiv. of water in THF at -78 °C afforded the bis(phenolate) lanthanide hydroxides as dimers [{(MBMP)Ln(µ-OH)(THF)₂}] [Ln = Nd (1), Yb (2)] in high yields. Complexes 1 and 2 reacted with phenyl isocyanate in THF, after workup, to give the desired O–H addition products, [(MBMP)Ln(µ- $\eta^{1:}\eta^{2-}O_2$ CNHPh)(THF)₂]₂ [Ln = Nd (3), Yb (4)] in excellent isolated yields. These complexes were well characterized, and the molecular structures of complexes 2 to 4 were determined by X-ray crystallography. The ytterbium atom in complex 2 is coordinated to six oxygen atoms to form a distorted octahedral geometry, whereas each metal center in complexes 3 and 4 is seven-coordinated, and the coordination geometry can be best described as a distorted pentagonal bipyramid.

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1. Introduction

Carbon-bridged bis(phenol)s, such as 2,2'-methylene-bis(6-tertbutyl-4-methylphenol) (MBMPH₂) and 2,2'-ethylidene-bis(4,6-ditert-butylphenol) (EDBPH₂), have been used in transition and main group metal coordination chemistry for a long time. These ligands have been found to be able to act as dianionic ligands, which have the advantage of providing a stereochemically rigid framework for the metal center that could affect stereospecific transformations. Meanwhile, some of these transition and main group metal complexes have shown great potential application in homogeneous catalysis [1–13]. In contrast, the synthesis and reactivity of lanthanide complexes stabilized by carbon-bridged bis(phenolate) groups has seldom been studied.

Our recent studies have demonstrated that the carbon-bridged bis(phenolate) lanthanide complexes also have interesting reactivity [14–19]. For example, the neutral trivalent lanthanide alkoxo complexes based on these ligand systems can initiate efficiently the ring-opening polymerization of ε -caprolactone in a controlled manner [15,17]; the neutral and anionic lanthanide amides stabilized by the MBMP^{2–} group can be synthesized in a controlled manner using [(MBMP)Ln(μ -Cl)(THF)₂]₂ as the precursors by tuning of the molar ratio of the reagents, and the neutral bis(phenolate) lanthanide amides [(MBMP)Ln{N(SiMe₃)₂(THF)₂] cannot

only initiate efficiently *ɛ*-caprolactone polymerization, but also activate carbodiimide to give lanthanide guanidinate complexes [18]. During our further study of the reactivity of [(MBMP)Nd{N(Si- Me_{3}_{2} (THF)₂ with phenyl isocyanate, an unexpected by-product $[{(MBMP)Nd(\mu-\eta^1:\eta^2-O_2CNHPh)(THF)_2}_2]$ was isolated. The proposed formation mechanism of this complex is that the partial hydrolysis of bis(phenolate) neodymium amide forms the corresponding neodymium hydroxide first, and then phenyl isocyanate inserts to the O-H bond to form the final product as shown in Scheme 1. Although the lanthanide hydroxides have been known for a long time, to our best knowledge, there is only one paper which reported the regioselective transformation of the hydroxo group of the organolanthanide hydroxides. Zhou et al. recently reported the reactivity of the lanthanocene hydroxides toward some small molecules [20]. This promoted us to study the synthesis and reactivity of bis(phenolate) lanthanide hydroxides. Here we report the results.

2. Results and discussion

2.1. Synthesis and characterization of bis(phenolate) lanthanide hydroxides

In order to confirm the above postulation, we intend to synthesize the bis(phenolate) lanthanide hydroxides and explore their reactivity toward phenyl isocyanate. Our previous work has demonstrated that carbon-bridged bis(phenolate) lanthanide



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cyclopentadienyl complexes, $[(MBMP)Ln(C_5H_5)(THF)_n]$, are good precursors for the synthesis of the corresponding lanthanide derivatives via protic exchange reactions and a partial hydrolysis product was isolated [15,19]. Thus, $[(MBMP)Ln(C_5H_5)(THF)_n]$ were used as starting materials to synthesize the bis(phenolate) lanthanide hydroxides by controlled hydrolysis reaction. $[(MBMP)Ln(C_5H_5)(THF)_2]$ (Ln = Nd, Yb) reacted with distilled water in THF in a 1:1 molar ratio at -78 °C. the color of the solution changed gradually from blue to pale blue (for neodymium) or yellow to pale yellow (for ytterbium). After workup, pale blue (complex 1) or pale yellow (complex 2) microcrystals were obtained in good isolated yields. Elemental analysis results revealed that these complexes consist of one dianionic bis(phenolate) group ($MBMP^{2-}$), one hydroxide, and two coordinated THF molecules at the metal center. Their IR spectra show the characteristic absorption bands of hydroxo group at about 3605 cm⁻¹, and aromatic rings in the region 1400–1600 cm⁻¹ (skeletal vibrations). Further molecular structure determination of complex 2 confirmed that they have solvated dimeric structures [{(MBMP)Ln(μ -OH)(THF)₂}] [Ln = Nd (1), Yb (2)] as shown in Scheme 2.

The molecular structure of complex **2** is shown in Fig. 1, and its selected bond lengths and angles are listed in Table 1. Complex **1** has a dimeric structure, and two molecules are connected together by two bridged hydroxo groups. The molecule has approximate C_2 symmetry. Each ytterbium atom is six-coordinated with two oxygen atoms from one bridged bis(phenolate) group, two oxygen atoms from two bridged hydroxo groups and two oxygen atoms from two THF molecules. The coordination geometry at ytterbium atom can be described as a distorted octahedron, in which O(1), O(2), O(5) and O(6) can be considered to occupy the equatorial positions, and O(7) and O(8) to occupy the apical positions, and the angle of O(7)–Yb–O(8) is distorted away from the idealized 180° to 171.9(2)°.

The average Yb–O(Ar) bond length of 2.085(6) Å falls in the range of Yb–O(Ar) bond lengths in other carbon-bridged bis(phenolate) ytterbium complexes, such as [{(MBMP)₂Yb(μ -OPrⁱ)(THF)₂}₂] [15], [Li(THF)₄][(MBMP)Yb{N(SiMe₃)₂}₂], and [{(MBMP)Yb(μ -Cl)(THF)₂}₂] [18] [2.059(2)–2.120(3) Å]. The Yb–O(H) bond lengths range from 2.211(4) to 2.241(4) Å, giving the average of 2.227(5) Å, which is comparable well with the corresponding bond lengths in [{(MBMP)₂Yb(THF)₂}₂(μ -OCH₂Ph)(μ -OH)] [2.211(4) Å] [15], [{Yb(OC₆H₃-2,4,6-Bu^t₃)₂(μ -OH)(THF)}₂] [2.208(6) Å] [21], [{Yb(OC₆H₃-2,6-Bu^t₂)₂(μ -OH)(THF)}₂] [2.217(7) Å] [22] and [(Me₃SiC₅H₄)₂Yb(μ -OH)₂] [2.29(2) Å] [23]. The most



Scheme 2.

remarkable feature of the structure of complex **2** is that there is remote O-H...Yb interaction involving the hydroxide hydrogen atom. The Yb(2)–H(5A) bond length of 2.75(4) Å is significantly longer than the Ln–H bond lengths in most of the organolanthanide hydrides [24,25], but it accords with the Lu(1)–H(2) of 2.70(5) Å in [{(C₅Me₄SiMe₃)LuH₂}] [25], and Y(1)–H(16e) of 2.935(6) Å in [(C₅Me₅)Y(OC₆H₃^{*i*}Bu₂)CH(SiMe₃)₂] [26].

2.2. Reactivity with phenyl isocyanate

Reactions of complexes **1** and **2** with phenyl isocyanate in THF, after workup, gave the desired O–H addition products, [{(MBMP) $Ln(\mu-\eta^1:\eta^2-O_2CNHPh)(THF)_2$]2 [Ln = Nd (**3**), Yb (**4**)] in excellent isolated yields as shown in Scheme 3. Complexes **3** and **4** were characterized by elemental analysis and IR spectroscopy, and their definitive molecular structures were provided by single-crystal X-ray diffraction. These reactions are quite different from those of lanthanocene hydroxides with phenyl isocyanate reported by Zhou et al. and complexes **3** and **4** can be considered as the proposed intermediate species (II) in the latter [20]. Attempts to eliminate the N–H proton with [(C_5H_5)_3Ln(THF)] as that reported by Zhou were unsuccessful, and the isolated compound is the starting material. These results revealed that the ancillary ligands have a profound effect on the reactivity of the corresponding lanthanide complexes.

Complexes **3** and **4** are isostructural, and only the molecular structure of complex **3** is shown in Fig. 2, and their selected bond lengths and angles are provided in Table 2. Both complexes have solvated C₂ symmetric dimeric structures. Two molecules are connected together by two bridged oxygen atoms from carbaminate groups PhNHCO₂, and the eight atoms Nd(1), O(3), C(24), O(4), Nd(1A), O(3A), C(24A), and O(4A) form an interlinked tricyclic structure via the two bridged Nd-O bonds [Nd(1)-O(3A) and Nd(1A)-O(3)]. The corn structure is similar to those of $[{(CH_3C_5H_4)_2Y(\mu \eta^{1}:\eta^{2}-S_{2}CNPh_{2})_{2}$ [27], and [{Cp₂Ln(μ - $\eta^{1}:\eta^{2}-O_{2}CCHEtPh$)}₂] (Ln = Yb, Er, Y) [20], but different from that of $[{(C_5Me_5)_2Sm(\mu O_2$ CEPh) $_2$ [28]. Each central metal atom is seven-coordinated by two oxygen atoms from one bridged bis(phenolate) ligand, and one oxygen atom from a PhNHCO₂ group, and two oxygen atoms from another PhNHCO₂ group, and two oxygen atoms from two THF molecules. The coordination geometry around the central metal atom can be described as a distorted pentagonal bipyramid, in which O(1), O(5), O(4A), O(3A) and O(3) can be considered to occupy the equatorial positions with the sum of the bond angles of 360.2° in complex **3**, and 359.7° in complex **4**, respectively, and O(2) and O(6) to occupy the axis positions. The bond angles of O(2)-Ln-O(6) are slightly distorted away from the ideal value of 180° to $164.6(1)^{\circ}$ in complex **3**, and $162.8(1)^{\circ}$ in complex **4**, respectively.

The Nd–O(Ar) bond distances are 2.267(3) and 2.154(4) Å, giving the average of 2.210(4) Å, which is very close to those observed in related neodymium complexes $[{(MBMP)_2Nd(\mu-OPr^i)(THF)_2}_2]$ [2.215(6) Å] [15], $[{(EDBP)Nd(\mu-O^iPr)(THF)_2}]$ [2.225(5) Å] [17], $[(MBMP)Nd{N(TMS)_2}(THF)_2]$ [2.200(2) Å], and $[Li(THF)_4]$ $[(MBMP)Nd{N(TMS)_2}_2]$ [2.195(3) Å] [18]. The carbaminate group is asymmetrically coordinated to the neodymium atom with the var-



Fig. 1. ORTEP diagram of complex 2 showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1Selected bond distances (Å) and angles (°) for complex 2.

Bond distance			
Yb(1) - O(1)	2.085(4)	Yb(2)–O(3)	2.078(4)
Yb(1) - O(2)	2.088(4)	Yb(2)–O(4)	2.090(4)
Yb(1) - O(5)	2.221(4)	Yb(2)–O(5)	2.241(4)
Yb(1) - O(6)	2.237(4)	Yb(2)–O(6)	2.211(4)
O(1) - C(1)	1.344(6)	O(3)-C(24)	1.338(6)
O(2)-C(7)	1.351(6)	O(4)-C(30)	1.340(6)
Bond angle			
O(1) - Yb(1) - O(2)	97.4(2)	O(3) - Yb(2) - O(4)	97.8(2)
O(2) - Yb(1) - O(6)	88.8(2)	O(4) - Yb(2) - O(5)	90.6(2)
O(5) - Yb(1) - O(6)	71.7(1)	O(5) - Yb(2) - O(6)	71.9(1)
O(1) - Yb(1) - O(5)	102.9(1)	O(6) - Yb(2) - O(3)	100.8(2)
O(8) - Yb(1) - O(7)	171.9 (2)	O(9)-Yb(2)-O(10)	172.7(1)

iation in Nd–O bond lengths of about 0.07 Å [2.493(3) and 2.563(3) Å, respectively], which is similar to those found in [$\{Cp_2Ln(\mu-\eta^{1}:\eta^{2}-O_2CCHEtPh)\}_2$] (Ln = Yb, Er, Y) [20]. The Nd–O(3) bond length of 2.395(3) Å is comparable with the averaged bridged Nd–O(Ar) bond length in neodymium bis(phenolate) guanidinate complex [$\{(\mu$ -O-MBMP)Nd[(ⁱPrN)_2CN(TMS)_2]\}_2] (2.401 Å) [18], but is apparently smaller than the bond lengths of Nd–O(3A) [2.493(3) Å] and Nd–O(4A) [2.563(3) Å]. The latter compare well with the bond lengths of Nd–O(THF) [2.458(3) and 2.567(4) Å], which revealed that these bonds are donating bond of neutral oxygen-donor ligands. It is worthy to note that the bridged Nd–O(3A) bond is shorter than the terminal Nd–O(4A) bond, which is quite different from those in [$\{Cp_2Ln(\mu-\eta^{1}:\eta^{2}-O_2CCHEtPh)\}_2$] (Ln = Yb, Er, Y) [20]. Gen-



Fig. 2. ORTEP diagram of complex **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and carbon atoms of THF molecules are omitted for clarity. Complex **4** is isostructural with complex **3**.

erally, the bridged bond is longer than the terminal one. The shorter bridged Nd–O bond length in our case might be attributed to the relatively weak electron delocalization within the carbaminate group. Because the C(24)-O(4) bond length of 1.249(6) Å falls in the range



Scheme 3.

	3	4		3	4	
Bond length						
Ln(1) - O(1)	2.267(3)	2.157(3)	Ln(1) - O(2)	2.154(4)	2.068(3)	
Ln(1) - O(3)	2.395(3)	2.285(3)	Ln(1)-O(3A)	2.493(3)	2.368(3)	
Ln(1)-O(4A)	2.565(3)	2.421(3)	Ln(1)-O(5)	2.458(3)	2.326(3)	
Ln(1) - O(6)	2.567(4)	2.407(4)	Ln(1)-C(24A)	2.924(5)	2.780(5)	
O(3)-C(24)	1.307(5)	1.308(6)	O(4)-C(24)	1.249(6)	1.240(6)	
Bond angle						
O(2) - Ln(1) - O(6)	164.6(1)	162.8(1)	O(1)-Ln(1)-O(5)	87.7(1)	84.9(1)	
O(5) - Ln(1) - O(4A)	76.1(1)	76.3(1)	O(4A)-Ln(1)-O(3A)	51.7(1)	54.4(1)	
O(3A) - Ln(1) - O(3)	64.9(1)	64.5(1)	O(3) - Ln(1) - O(1)	79.8(1)	79.6(1)	
Ln(1) - O(3) - Ln(1A)	115.2(1)	115.6(1)				

 Table 2

 Selected bond distances (Å) and angles (°) for complexes 3 and 4

of C=O double bond and the C(24)–O(3) bond length of 1.307(5) Å falls in the range of C–O single bond, and the deviation of their bond distances is apparently larger than the corresponding values found in [{Cp₂Ln(μ - η^1 : η^2 -O₂CCHEtPh)}₂] (Ln = Yb, Er, Y) [20]. There is a strong π interaction of the carbon atom of the carbaminate group with the neodymium atom. The Nd–C(24A) bond length of 2.924(5) Å is apparently lower than the Nd–C contact observed in [{(MBMP)Nd(μ -OⁱPr)(THF)₂}₂] [3.101(7) Å] [15] and compares well with those observed in the neutral arene neodymium complexes [Nd(η^6 -C₆H₆)(AlCl₄)₃] [2.933(18) Å] [29], [Nd(η^6 -C₆H₅Me)(AlCl₄)₃] [2.926(5) Å] [30], and [Nd(η^6 -1,3,5-C₆H₃Me₃)(AlCl₄)₃] [2.916(9) Å] [31], in which the Nd–C π interaction was considered to exist unambiguously.

In complex **4**, the average Yb–O(Ar) bond length is 2.112(3) Å, which accords with those found in the carbon-bridged bis(phenolate) lanthanide complexes mentioned above when the difference in ionic radii is considered. The Yb–O(3) bond distance of 2.285(3) Å is also apparently smaller than the Yb–O(3A) and Yb– O(4A) bond distances, which revealed the Yb–O(3A) and Yb– O(4A) bond are donating bond. The Yb–C(24A) bond length of 2.780(5) Å compares well with that in complex **3**, when the difference in ionic radii is considered, but apparently lower than that

 Table 3

 Details of the crystallographic data and refinements for complexes 2-4.

Compound	2 · 3.5THF	$\bm{3}\cdot 2C_7H_8$	$\bm{4}\cdot 2C_7H_8$
Formula	C ₇₆ H ₁₂₂ O _{13.50} Yb ₂	$C_{90}H_{120}N_2Nd_2O_{12}$	C ₉₀ H ₁₂₀ N ₂ O ₁₂ Yb ₂
Formula weight	1597.81	1710.36	1767.96
T (K)	293(2)	193(2)	193(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	ΡĪ	$P2_1/n$	$P2_1/n$
a (Å)	13.081(1)	14.398(2)	14.064(2)
b (Å)	15.570(1)	17.475(2)	17.228(3)
c (Å)	19.844(2)	17.148(2)	17.453(3)
α(°)	85.319(5)		
β (°)	87.009(5)	102.362(3)	99.842(3)
γ(°)	80.354(4)		
V (Å ³)	3968.0(6)	4214.4(8)	4166.7(11)
Ζ	2	2	2
$D_{\rm calc} ({\rm g}/{\rm cm}^{-3})$	1.336	1.348	1.409
μ (mm ⁻¹)	2.399	1.278	2.291
F(000)	1650	1780	1820
Crystal size (mm)	$0.80 \times 0.48 \times 0.39$	$0.50 \times 0.40 \times 0.20$	$0.60\times0.48\times0.20$
2θ range (°)	50.7	50.7	50.7
Reflections collected	37676	40212	39220
Independent reflections	14415	7698	7611
Reflections with $I \ge 2.0\sigma(I)$	11882	6591	6685
Parameters refined	829	512	488
GOF	1.109	1.185	1.145
R	0.0471	0.0546	0.0456
wR	0.1033	0.1103	0.0968

found in the neutral arene ytterbium complex $[Yb(\eta^{6}-1,3,5-C_6Me_6)(AlCl_4)_3]$ [2.87(4) Å] [32], which indicating the presence of strong π interaction. Similar to that in complex **3**, the terminal Yb–O(4A) bond is longer than the bridged Yb–O(3A) bond.

3. Conclusion

In summary, the lanthanide hydroxides stabilized by a carbonbridged bis(phenolate) ligand were prepared, and their reactivity toward phenyl isocyanate was explored. The structural properties of some of these complexes were provided by X-ray diffraction. Controlled hydrolysis of bis(phenolate) lanthanide cyclopentadienyl complexes in THF at low temperature gave the corresponding lanthanide hydroxides as dimers. These lanthanide hydroxo complexes reacted with phenyl isocyanate in THF to give the desired O–H addition products, which provided an alternative route to synthesize lanthanide carbaminate complexes. In comparison with the final products of the reactions of lanthanocene hydroxides with phenyl isocyanate, theses results revealed that the ancillary ligands have a profound effect on the reactivity of the corresponding lanthanide complexes.

4. Experimental

4.1. Materials and methods

All of the manipulations described below were performed under an argon atmosphere, using the standard Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over sodium or sodium benzophenone ketyl and distilled under argon prior to use. $[(MBMP)Ln(C_5H_5)(THF)_2]$ were prepared according to the literature methods [15,19]. The other reagents were purchased from Acros and used as received without further purification. Metal analyses were carried out using complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo Erba-1110 instrument; Quoted data are the average of at least two independent determinations. IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

4.2. Synthesis of $[{(MBMP)Nd(\mu-OH)(THF)_2}_2]$ (1)

A solution of $[(MBMP)Nd(C_5H_5)(THF)_2]$ (1.47 g, 2.13 mmol) in THF (30 mL) was cooled to -78 °C. The solution was stirred half an hour, and then a THF solution (30 mL) containing distilled water (38 mg, 2.13 mmol) was added dropwise. The color of the solution was changed gradually from blue to pale blue. The mixture was stirred for 2 h, and then warmed to room temperature and stirred overnight. Little precipitate was separated by centrifugation, and the resulting pale blue solution was concentrated to about 18 mL. Pale blue microcrystals were obtained at room temperature in a few days (0.97 g, 71%), m.p.: 176–178 °C (dec). *Anal. Calc.* for $C_{62}H_{94}Nd_2O_{10}$: C, 57.82; H, 7.36; Nd, 22.40. Found: C, 57.58; H, 7.81; Nd, 22.66%. IR (KBr pellet, cm⁻¹): 3607(m), 3385(m), 2955(s), 2913(m), 1605(m), 1461(s), 1433(s), 1350(m), 1212(s), 1158(s), 867(w), 729(w).

4.3. Synthesis of $[{(MBMP)Yb(\mu-OH)(THF)_2}_2]$ (2)

The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but $[(MBMP)Yb(C_5H_5)(THF)_2]$ (1.34 g, 1.86 mmol) was used instead of $[(MBMP)Nd(C_5H_5)(THF)_2]$. Pale yellow microcrystals were obtained at room temperature in a few days (0.75 g, 60%), m.p.: 180–182 °C (dec). *Anal. Calc.* for $C_{62}H_{94}O_{10}Yb_2$: C, 55.35; H, 7.04; Yb, 25.72. Found: C, 55.60; H, 7.10; Yb, 25.42%. IR (KBr, cm⁻¹): 3605(m), 3389(m), 2956(s), 2916(m), 1605(m), 1464(s), 1434(s), 1353(m), 1213(s), 1156(s), 864(w), 728(w). The crystals suitable for an X-ray crystal structure determination were obtained in THF solution at room temperature.

4.4. Synthesis of [{(MBMP)Nd(μ - η^1 : η^2 -O₂CNHPh)(THF)₂]₂] (**3**)

A Schlenk flask was charged with complex **1** (0.77 g, 0.60 mmol) and THF (30 mL). Phenyl isocyanate (PhNCO) (0.65 mL, 1.20 mmol) was added by syringe. The reaction mixture was stirred overnight at room temperature. After removed the volatiles under reduced pressure, the pale blue residue was washed with cooled THF twice. The pale blue powder was dried at room temperature (0.77 g, 84%), m.p.: 218–220 °C (dec). *Anal. Calc.* for $C_{76}H_{104}N_2Nd_2O_{12}$: C, 59.81; H, 6.87; N, 1.83; Nd, 18.90. Found: C, 59.41; H, 6.42; N, 1.95; Nd, 19.11%. IR (KBr, cm⁻¹): 3346(w), 2953(m), 2904(m), 1616(s), 1590(s), 1538(vs), 1445(s), 1337(m), 1298(s), 1239(m), 1024(m), 864(m), 779(m). The crystals suitable for an X-ray crystal structure determination were obtained by recrystallization from THF-toluene solution at room temperature.

4.5. Synthesis of [{(MBMP)Yb(μ - η^1 : η^2 -O₂CNHPh)(THF)₂]₂] (**4**)

The synthesis of complex **4** was carried out in the same way as that described for complex **3**, but complex **2** (0.67 g, 0.50 mmol) was used instead of complex **1**. Pale yellow powder was obtained at room temperature (0.64 g, 81%), m.p.: 198–200 °C (dec). *Anal.* Calc. for $C_{76}H_{104}N_2O_{12}Yb_2$: C, 57.64; H, 6.62; N, 1.77; Yb, 21.85. Found: C, 57.39; H, 6.50; N, 1.91; Yb, 21.54%. IR (KBr, cm⁻¹): 3347(w), 2953(m), 2905(m), 1617(s), 1591(s), 1538(vs), 1446(s), 1338(m), 1298(s), 1239(m), 1025(m), 864(m), 780(m). The crystal suitable for an X-ray crystal structure determination were obtained by recrystallization from THF-toluene solution at room temperature.

4.6. X-ray structures determination

Suitable single-crystals of complexes **2**–**4** were sealed in a thinwalled glass capillary for determination the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo K α radiation (λ = 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 3.

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. 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.

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Appendix A. Supplementary data

CCDC 700053, 700054 and 700055 contain the supplementary crystallographic data for complexes **2–4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.11.031.

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