Ytterbium amides of linked bis(amidinate): synthesis, molecular structures, and reactivity for the polymerization of L-lactide[†]

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Received 19th June 2007, Accepted 31st August 2007 First published as an Advance Article on the web 10th September 2007 DOI: 10.1039/b709310a

The steric effect of an amide group on the synthesis, molecular structures and reactivity of ytterbium amides supported by linked bis(amidinate) L (L = $[Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3]$) is reported. Reaction of LYbCl(THF)₂ with equimolar NaNHAr' and NaNHAr (Ar' = 2,6-Me₂C₆H₃; Ar = 2,6-iPr₂C₆H₃), respectively, gave the corresponding monometallic amide complexes LYb(NHAr')(DME) **1** and LYb(NHAr)(DME) **2**, in which the linked bis(amidinate) is coordinated to the metal center as a chelating ligand. The similar reaction with NaN(SiMe₃)₂ afforded a bimetallic amide complex (TMS)₂NYb(L)₂YbN(TMS)₂ **3** formed through the rearrangement reaction of L induced by the bulky N(SiMe₃)₂ group. In complex **3** the two linked bis(amidinate)s act as bridging ancillary ligands to link two YbN(TMS)₂ species in one molecule. The definite molecular structures of **1–3** were provided by single-crystal X-ray analysis. Complexes **1–3** are efficient initiators for the polymerization of L-lactide, and their catalytic performance is highly dependent on the amido groups and molecular structures. The polymerizations initiated by complexes **1** and **2** proceeded in a living fashion as evidenced by the narrow polydispersities of the resulting polymers, together with the linear natures of the number average molecular weight *versus* conversion plots, while the polymerization system with complex **3** provided polymers with rather broad molecular weight distributions.

Introduction

There is currently considerable interest in developing structurally well-characterized lanthanide complexes as homogeneous catalysts for the ring-opening polymerization of lactide, due to the biodegradable and biocompatible nature of polylactides and their wide applications in medicine, pharmaceutics and tissue engineering.¹ Lanthanide alkoxides are well-known to be highly efficient initiators for the ring-opening polymerization of lactide.² In particular, lanthanide alkoxides supported by polydentate ligands, such as tetradentate bis(phenolate) containing heteroatoms "ONNO",²e "ONOO",^{2d,2e} exhibit a high degree of control over the polymerization of lactide especially of the stereochemistry of the lactide polymerization.^{2d,2e}

Lanthanide amide complexes are another class of initiators which have recently attracted much attention.^{2d,2e,3} A growing number of structurally characterized silylamide complexes were synthesized and found to initiate lactide polymerization with high reactivity.^{2d,2e,3a-3f} However, only some of the lanthanide amide initiators afforded polylactides with predicted molecular weights and narrow molecular weight distributions. These were the amides bearing tetradentate bis(phenolate) "ONOO",^{2d,3d} "ONOO",^{2d} and "OSSO".^{3e,3f} The catalytic performance of lanthanide amides is well-known to depend on both amide, being the initiating group, and the ancillary ligand around the metal center which tunes the catalytic activity, controllability and selectivity by virtue

of its steric and electronic effect. So, there is much scope for designing novel lanthanide amides as efficient initiators in lactide polymerization.

Linked bis(amidinate)s are an alternative "NNNN" tetradentate ligand. The synthesis of the monomeric yttrium alkyl complex, LYCH(SiMe₃)₂(THF)₂ ($L = [Me_3SiNC(Ph)N(CH_2)_3NC-(Ph)NSiMe_3]$), was first reported in 2001,⁴*a* then the analogous cyclopentadienyl ytterbium complex, LYbCp(DME), was synthesized by us.⁴*b* However, the application of this class of ligand in designing lanthanide complexes as efficient initiators has been ignored to date. Here we would like to report novel lanthanide amide initiators for controlled polymerization of L-lactide by the combination of a linked bis(amidinate) ligand with a ytterbium amide unit. The synthesis of these amide complexes and the effect of the amido group on the molecular structures will be presented.

Results and discussion

Synthesis and characterizations of complexes 1-3

The reaction of LYbCl(THF)₂,⁴⁶ which was synthesized according to the literature method, with 1 equiv. of sodium amide, NaNHAr' (Ar' = 2,6-Me₂C₆H₃), took place smoothly and a color change from light yellow to orange was immediately observed. After removal of NaCl and treatment with DME the reaction mixture afforded the DME-solvated amide complex 1 as yellow crystals in 55% yield upon crystallization (Scheme 1). The addition of DME facilitated crystallization. The same metathesis reaction with the more bulky amide salt, NaNHAr (Ar = 2,6-ⁱPr₂C₆H₃), yielded the analogous amide complex **2** as orange crystals in 60% yield (Scheme 1). IR spectra of both complexes showed a strong absorption of C=N stretch at approximately 1640 cm⁻¹ indicating

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[†]CCDC reference numbers 622179, 651215 and 651216. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709310a



the delocalized double bond of the N–C–N linkage.⁵ ¹H NMR spectra for both complexes were not available as ytterbium(III) is paramagnetic.

The same structural motif, with a chelating linked bis(amidinate) ligand, for **1** and **2** was further confirmed by X-ray diffraction analysis. Their solid state structures are shown in Fig. 1 and 2, respectively. Selected bond parameters are listed in Table 1. The central metal in each complex coordinates to four



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

Table 1 Selected bond lengths (Å) and bond angles (°) for complexes 1 and 2

	1	2
Yb(1)–N(1)	2.491(5)	2.432(4)
Yb(1)-N(2)	2.301(5)	2.317(3)
Yb(1) - N(3)	2.448(5)	2.514(4)
Yb(1) - N(4)	2.307(4)	2.287(4)
Yb(1)-N(5)	2.229(4)	2.214(3)
Yb(1)-C(1)	2.776(5)	2.738(4)
Yb(1)-C(2)	2.780(5)	2.814(4)
N(1)-C(1)	1.343(7)	1.344(6)
N(2)-C(1)	1.312(7)	1.317(6)
N(3) - C(2)	1.341(7)	1.333(5)
N(4)–C(2)	1.324(7)	1.317(6)
N(2)-Yb(1)-N(1)	56.11(15)	56.88(12)
N(4) - Yb(1) - N(3)	56.62(15)	55.48(12)
N(5)-Yb(1)-O(2)	149.91(16)	147.63(12)



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

nitrogen atoms from the chelating linked bis(amidinate) ligand, one nitrogen atom from the amide group and two oxygen atoms from a solvated DME molecule to adopt a distorted trigonal bipyramidal geometry, if the amidinate ligand is considered to occupy a single coordination vertex. The centers of the two amidinate groups and the oxygen atom O(1) occupy equatorial positions, while the nitrogen atom N(5) and the other oxygen atom O(2) are located at axial positions. The N(5)-Yb(1)-O(2)angle is distorted from the idealized 180° to 149.91(16)° for 1 and 147.63(12)° for 2. Almost no difference in the Yb–N(amidinate) bond distance between 1 and 2 was observed. In both complexes the amidinate groups are each unsymmetrically bound to the central metal in η^2 fashion through the nitrogen atoms in the Yb-N-C-N plane with a slight deviation (largest deviation is 0.0970 Å of plane Yb(1)–N(1)–C(1)–N(2) in complex 2). A substantial difference in Yb-N bond distance for the amidinate nitrogens attached to the bridge compared to those attached to the SiMe₃ group was observed for both complexes (the former being 0.171 Å shorter for 1, 0.166 Å for 2). The angle between the two Yb–N–C–N planes is 30.8° for 1 and 37.2° for 2 indicating a more open sphere around Yb both in 1 and 2 due to the chelating ancillary ligand. The same feature was found in the related complexes LY[CH(SiMe₃)₂](THF),^{4a} LYbC₅H₅(DME)^{4b} and a bridged aminotroponiminate lanthanum complex^{4c} reported previously. The Yb-N(amide) bond distance of 2.214(3) Å for 1 and 2.229(4) Å for 2 is slightly shorter than those for the ytterbium amide complexes reported previously,⁶ when the difference in ionic radii amongst Yb metals with different coordination numbers is considered.

Treatment of LYbCl(THF)₂ with the most bulky amide salt NaN(SiMe₃)₂ in comparison with NaNHAr' and NaNHAr (Ar' = $2,6-Me_2C_6H_{3}$; Ar = $2,6-Pr_2C_6H_{3}$) mentioned above generated the bimetallic amide complex **3** as colorless crystals in 56% yield upon crystallization (Scheme 1). The identity of **3** was established by X-ray crystallography (discussed below), although ¹H NMR spectra of **3** were unavailable due to the paramagnetism of

ytterbium(III). Obviously, the formation of 3 indicates that a ligand rearrangement reaction occurred during the metathesis reaction. A ligand rearrangement reaction for a bridged bis(amidinate) ligand has never been reported before, although a similar ligand rearrangement reaction for a linked bis(cyclopentadienyl) ligand was described previously.7,8 The occurrence of the ligand rearrangement reaction in our case may be attributed to the overcrowded environment around the central metal which would result upon formation of the corresponding monometallic amide, LYbN(SiMe₃)₂, due to the steric hindrance induced by the bulky $N(SiMe_3)_2$ group. The same reaction pathway as that described for the bimetallic lanthanocene hydride^{7,8} was proposed to explain the formation of 3. The attack of $NaN(SiMe_3)_2$ results in the cleavage of one of the linked bis(amidinate)-Yb bonds, followed by rearrangement to another Yb atom. The linked bis(amidinate) ligand here acts as bridging linked dianions to link the two Yb-NTMS moieties in one molecule. Such a coordination mode for a linked bis(amidinate) with a flexible – CH₂CH₂- bridge was found previously in a bimetallic titanium complex meso/rac-{CpTi(Me)₂[N(^tBu)C(Me)N(CH₂CH₂)-]}₂.⁹ In that case the bimetallic titanium complex was formed from the reaction of an α,ω -bis(carbodiimide) with two equiv. of CpTiMe₃ by CH₄ elimination.

Crystals of 3 suitable for an X-ray structure determination were obtained from a mixture of hexane– Et_2O . The molecular structure of 3 is shown in Fig. 3. Selected bond parameters are listed in Table 2. Complex 3 has a bimetallic structure, in



Fig. 3 OPTEP diagram of complex **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms and free solvent are omitted for clarity.

 Table 2
 Selected bond lengths (Å) and bond angles (°) for complex 3

N(2A) $Vb(1A)$ $N(1A)$	50.0(4)	N(2A) = N(AA)	50.7(4)
Yb(1A)–N(1A) Yb(1A)–N(2A) Yb(1A)–N(5A) Yb(1A)–N(6A) Yb(1A)–N(9A)	2.30(1) 2.30(1) 2.28(1) 2.29(1) 2.18(1)	Yb(2A)-N(3A) Yb(2A)-N(4A) Yb(2A)-N(7A) Yb(2A)-N(8A) Yb(2A)-N(10A)	2.26(1) 2.31(1) 2.30(1) 2.31(1) 2.19(1)

which the two Yb-NTMS groups are linked together by the two bridged bis(amidinate) ligands. The overall geometry of the molecule can be described as a boat-like structure with two amide groups lying on the same up sites. Each metal coordinates to two amidinate groups from the two bridging linked bis(amidinate) ligands and one nitrogen atom from the amide group to form a trigonal planar structure with the bisector of the amidinate ligands (Yb(1A)–C(1A) and Yb(1A)–C(24A); Yb(2A)–C(2A) and Yb(2A)-C(25A) vectors) defining two vertices and the metalamide linkage defining the third vertex. The angles defined by these vectors sum to 360°. All Yb-N distances for the amidinate nitrogen attached to the bridge and to SiMe₃ are around 2.29 Å for Yb(1A) and 2.30 Å for Yb(2A), no significant difference between them is observed, which is a marked contrast with those in 1 and 2, as well as in an alkyl yttrium complex,^{4a} but quite similar to those found in the bis(amidinate) complex, [(p- $MeOC_6H_4$)C(NSiMe_3)₂]₂Y[CH(SiMe_3)₂] **4**, supported by the two monoanionic amidinate ligands.⁹ The angles between the planes of Yb(1A)-N(1A)-C(1A)-N(2A) and Yb(1A)-N(5A)-C(24A)-N(6A) and the planes of Yb(2A)-N(7A)-C(25A)-N(8A) and Yb(2A)–N(3A)–C(2A)–N(4A) are 83.6° and 85.2° , respectively, which are much larger than 30.8° in 1 and 37.2° in 2. The angles are also larger than 75.6° for the related monometallic complex 4.¹⁰ The much larger angles found in complex 3 might be attributed to the demand of the bimetallic structure. This may also be the reason as to why 3 is a solvent free complex, while complexes 1 and 2 allow a coordinated DME molecule. The two Y-N(amide) bond distances are almost equal giving an average of 2.19 Å which is apparently shorter than 2.34 Å found in monometallic guanidinate amide [C₆H₁₁NC(N(SiMe₃)₂)NC₆H₁₁]₂YbN(SiMe₃)₂,¹¹ but longer than that found in complexes 1 (2.21 Å) and 2 (2.23 Å), taking into account the difference in ionic radii resulting from the different coordination number. The bimetallic structure of 3 in comparison with 1 and 2 shows that coordinate geometry of a linked bis(amidinate) can be modified by using a different steric bulky reagent.

Polymerization of L-lactide initiated by complexes 1-3

All complexes have been tested as initiators for the polymerization of L-lactide. The results obtained under various conditions are listed in Table 3. All the complexes were found to be highly active initiators for the polymerization of L-lactide in toluene. However, these complexes showed much lower reactivity in THF compared with that in toluene (Table 3, entries 7, 15, and 19), presumably because of competitive coordination between the monomer and THF.^{24/3c,3d}

To further address the influence of the amido group on the polymerization characterizations of lanthanide amides, a series of experiments was carried out at 60 °C in toluene. Complex 2 allowed complete conversion of 300 equiv. of L-lactide to polymer within 1 min at 60 °C in toluene at a concentration of L-lactide of 1 mol L⁻¹ (entry 8), while complexes 1 and 3 afforded the conversion of 54% and trace amounts respectively under the same conditions (entries 2 and 16). For complex 2 the polymer yield was still as high as 95% within 7 min though the molar ratio of monomer to initiator increased to 500 (entry 13). The activity sequence for the amido group is $-N(SiMe_3)_2 < -NHAr' < -NHAr$. The influence of the amido groups on the molecular weight

Table 3Polymerization of L-lactide initiated by complexes $1-3^a$

Entry	Initiator [I]	T∕°C	$[\mathbf{M}]_0 : [\mathbf{I}]_0^{\ b}$	t/min	Yield (%) ^c	$M_{\rm n} \times 10^{4d}$	$M_{\rm n} \times 10^{\rm 4e}$	PDI	
1	1	60	300	0.5	30	3.30	1.30	1.32	
2	1	60	300	1	54	6.10	2.33	1.33	
3	1	60	300	1.5	65	6.90	2.81	1.32	
4	1	60	300	3	92	10.9	3.97	1.35	
5	1	70	300	1	70	7.77	3.02	1.32	
6	1	80	300	1	85	9.20	3.67	1.25	
75	1	60	300	1			_		
8	2	60	300	1	100	4.10	4.32	1.31	
9	2	60	500	20 s	15	0.83	1.08	1.30	
10	2	60	500	1.5	50	3.80	3.60	1.30	
11	2	60	500	3	75	5.80	5.40	1.30	
12	2	60	500	5	89	6.32	6.41	1.26	
13	2	60	500	7	95	6.50	6.84	1.29	
14	2	60	600	5	23	2.79	1.98	1.22	
15⁄	2	60	300	1					
16	3	60	300	1	Trace				
17	3	60	300	5	60	3.30	2.59	1.89	
18	3	60	300	10	100	6.00	4.32	2.01	
19⁄	3	60	300	10					

^{*a*} General polymerization conditions: in toluene, $[LLA] = 1 \mod L^{-1}$. ^{*b*} $[M]_0 : [I]_0 = [monomer] : [initiator]$. ^{*c*} Yield: weight of polymer obtained/weight of monomer used. ^{*d*} Measured by GPC calibrated with standard polystyrene samples. ^{*e*} M_n value calculated from the relationship: molecular weight of M × conv. × $[M]_0/[I]_0$. ^{*f*} In THF.

and molecular weight distribution of the resulting polymers was also observed. All the polymers obtained by complexes 1-3have unimodal molecular weight distributions. However, the molecular weight distribution indices of the polymers are diverse, ranging from 1.22-2.01 depending on the complex used. The polymerization systems with complexes 1 and 2 gave polymers with narrow molecular weight distributions ranging from 1.22 to 1.35 (entries 1-6 and 8-14), while the polymerization by complex 3 yielded polymers with rather broad molecular weight distributions (1.89-2.01, entries 17 and 18). The reason for this may be because the former two complexes acted as singleactive site initiators, but complex 3 played the role of a doubleactive site initiator due to the two Yb-N(SiMe₃)₂ active groups participating in the initiation. The polydispersity indices of the polymers resulting from systems using initiators 1 and 2 are lower than the usual values found for lanthanide amides (ranging from 1.32-1.72)^{3b} indicating that the two systems have "living character". Moreover, a difference in the molecular weights of the polymers resulting from the system using complex 1 compared to those obtained with complex 2 was observed. The experimental number molecular weights obtained by complex 2 are close to the calculated values, while the experimental values for the case of complex 1 are larger than the calculated values (entries 1-6 and 8-14). This result indicated that polymerization with complex 2 proceeded in better controlled mode compared to the system with complex 1.

The polymerization kinetics at 60 °C in toluene with the molar ratio of monomer : initiator of 300 for **1** and 500 for **2**, respectively, were conducted. The conversion increased with polymerization time and the pseudo first order kinetic plots of $\ln([M]_0/[M])$ versus polymerization time were observed for both systems as shown in Fig. 4. The linear semi logarithmic plots indicate the concentration of the catalytically active species remained constant throughout the polymerization. In both cases the number average molecular weights (M_n) of the resulting



Fig. 4 Plot of reaction time versus $\ln[M]_0/[M]$ initiated by 1 and 2. Conditions: $[M]_0/[I]_0 = 300$ for 1; $[M]_0/[I]_0 = 500$ for 2, $[LA]_0 = 1$ mol, 60 °C, Ar.

polymers increased proportionally with the monomer conversions, while the molecular weight distributions (M_w/M_n) of the resulting polymers remained narrow $(M_w/M_n \le 1.35)$ and intact (Fig. 5). All the results indicated that the polymerization of lactide initiated by 1 and/or 2 proceeded in a controlled mode.

The controlled polymerization of lactide with lanthanide amides without addition of alcohol as an initiator was negligible. These results indicated that substantial differences in geometry and catalytic behavior can be achieved by the combination of a linked bis(amidinate) ligand and lanthanide active species.

Conclusion

We have synthesized and structural characterized ytterbium amides complexes 1–3 bearing chelating or bridged bis(amidinate)



Fig. 5 Plot of polymer yield *versus* M_n and M_w/M_n initiated by 1 and 2. Conditions are the same as in Fig. 4.

ligands depending on the amido group. For amido groups HNAr' and HNAr the monometallic complexes **1** and **2** with a linked bis(amidinate) ligand were synthesized, while for the bulky amido group N(SiMe₃)₂ the bimetallic complex **3** supported by two bridged bis(amidinate) ligands was prepared. Complexes **1** and **2** were found to initiate the polymerization of L-lactide in a controlled mode which was confirmed by the results of polymerization kinetics, and the linear relationship between molecular weights and conversions, and the narrow molecular weight distributions of the resulting polymers ($M_w/M_n = 1.22$ –1.35). The results presented here indicated linked bis(amidinate) ligand systems may have potential applications in designing controlled lanthanide catalyst for homogeneous catalysis.

Experimental

General

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon before use. L-Lactide was purchased from Acros. LYbCl(THF)₂^{4b} was prepared according to the literature procedure. All other reagents were purchased from Acros and used as received without further purification. The IR spectra were recorded on a Magna-IR 550 spectrometer. Melting points were determined in a sealed Ar-filled capillary tube, and uncorrected. Lanthanide analyses were carried out by complexometric titrations. Carbon, hydrogen and nitrogen analyses were preformed by direct combustion with a Carlo-Erba EA 1110 instrument. Molecular weight and molecular weight distributions were determined against polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-2 and HR-4). THF was used as an eluent at 30 °C.

Synthesis of LYb(NHAr')(DME) ($Ar' = 2,6-Me_2C_6H_3$) (1)

To a stirred solution of LYbCl(THF)₂ (1.55 g, 2 mmol) in THF (30 mL) was added a solution of NaNHAr' (2 mmol, 0.50 M) in THF. The reaction mixture was stirred for 48 h at room

temperature. The volatiles were removed under reduced pressure and the residue was extracted with hot DME (2 × 50 mL) and the volume of the extract reduced to 40 mL. Cooling the solution to 0 °C afforded the yellow crystals (0.89 g, 55% based on Yb), mp 163–165 °C (Found: C, 52.41; H, 6.95; N, 8.35; Yb, 21.39. C₃₅H₅₄N₅O₂Si₂Yb requires C, 52.15; H, 6.75; N, 8.69; Yb, 21.47); ν_{max}/cm^{-1} 2960 m, 1642 s, 1608 s, 1569 s, 1541 s, 1488 m, 1438 m, 1384 s, 1084 s, 899 w, 782 m, 746 m, 700 m (KBr pellet).

Synthesis of LYbNHAr (DME) (Ar = $2,6^{-i}Pr_2C_6H_3$) (2)

Following a procedure similar to that describe for the preparation of complex **1**, treatment of a solution of LYbCl(THF)₂ (1.55 g, 2 mmol) in THF (30 mL) with one equiv. of NaNHAr (2 mmol, 0.60 M) in THF afforded complex **2** as orange crystals (1.03 g, 60% based on Yb), mp 190–192 °C (Found: C, 54.61; H, 7.66; N, 8.41; Yb, 20.19. $C_{39}H_{62}N_5O_2Si_2Yb$: C, 54.33; H, 7.25; N, 8.12; Yb, 20.07); v_{max}/cm^{-1} 2947 m, 1642 s, 1607 s, 1567 m, 1541 s, 1467 m, 1437 m, 1384 s, 1084 s, 899 w, 781 m, 700 m (KBr pellet).

Synthesis of (TMS)₂NYb(L)₂YbN(TMS)₂ (3)

A solution of NaN(TMS)₂ (2 mmol, 1 M) in THF was added to a stirring solution of LYbCl(THF)₂ (1.55 g, 2 mmol) in THF (30 mL). The reaction mixture was stirred for 48 h at room temperature. The volatiles were removed under reduced pressure and the residue was extracted with Et₂O (2 × 40 mL). The volume of the extract was reduced to 10 mL followed by addition of 1 mL hexane. Cooling the solution to 0 °C for crystallization afforded complex **3** as colorless crystals (0.85 g, 56% based on Yb), mp 95–97 °C (Found: C, 46.56; H, 7.18; N, 8.91; Yb, 22.55. C₅₈H₁₀₄N₁₀Si₈Yb₂: C, 46.06; H, 6.93; N, 9.26; Yb, 22.88); ν_{max} /cm⁻¹ 2955 m, 1635 s, 1559 s, 1497 m, 1381 s, 1250 m, 1211 w, 964 w, 833 m, 779 m, 748 m, 702 m (KBr pellet).

Polymerization of L-lactide

A typical procedure for polymerization of L-lactide was performed in a 25 mL round-bottom flask. To a stirred solution of L-lactide (0.43 g, 3 mmol) in toluene (2.4 mL), a toluene solution of complex **2** (0.6 mL, $[M]_0 : [I]_0 = 500 : 1$) was added with a syringe. The reaction mixture was stirred for 7 min at 60 °C (Table 3, entry 13) and then quenched with an ethanol solution containing a small amount of hydrochloric acid (5%). The polymer precipitated from ethanol and was washed with ethanol three times and dried under vacuum (0.41 g, 95%).

X-Ray crystallography[†]

Diffraction data were collected on a Rigaku Mercury CCD area detector in ω scan mode using Mo-K α radiation ($\lambda = 0.71070$ Å). X-Ray quality crystals of **1**, **2** and **3**·0.75(Et₂O)·0.25(C₆H₁₄) were obtained directly from the above preparations. A yellow block of **1** with dimensions $0.60 \times 0.42 \times 0.30$ mm, an orange block of **2** with dimensions $0.62 \times 0.43 \times 0.17$ mm and a colorless block of **3** with dimensions $0.24 \times 0.15 \times 0.14$ mm were each mounted in a sealed capillary. Diffraction data were collected using the ω mode with a detector distance of 35 mm to the crystals. A total of 720 oscillation images for each were collected in the range $6.01^{\circ} < 2\theta < 50.70^{\circ}$ for **1**, $6.01^{\circ} < 2\theta < 50.70^{\circ}$ for **2** and $6.06^{\circ} < 2\theta < 50.70^{\circ}$

	1	2	$3 \cdot 0.75(Et_2O) \cdot 0.25(C_6H_{14})$	
Empirical formula	C35H54N5O2Si2Yb	$C_{39}H_{62}N_5O_2Si_2Yb$	$C_{62.5}H_{115}N_{10}O_{0.75}Si_8Yb_2$	
FŴ	806.05	862.16	1589.36	
T/K	223(2)	193(2)	193(2)	
Crystal system	Monoclinic	Monoclinic	Triclinic	
Space group	$P2_1/c$	$P2_1/c$	$P\overline{1}$	
a/Å	23.288(2)	24.670(3)	17.806(2)	
b/Å	8.6725(7)	8.9342(11)	18.419(3)	
c/Å	20.4441(19)	19.672(3)	29.290(5)	
$a/^{\circ}$	90	90	80.666(8)	
β/°	111.162(2)	104.525(3)	72.924(8)	
y/°	90	90	66.204(7)	
$V/Å^3$	3850.6(6)	4197.1(9)	8392(2)	
Z	4	4	4	
$D_{\rm c}/{ m mg}~{ m m}^{-3}$	1.390	1.364	1.290	
R(int)	0.0403	0.0481	0.0888	
No. of reflns. colled.	36132	39 439	58 140	
No. of indep. colled.	7051	7639	30 041	
GOF	1.189	1.154	1.091	
R	0.0477	0.0368	0.1022	
wR	0.0945	0.0746	0.1740	

 Table 4
 Details of the crystallographic data and refinements for complexes 1–3

for **3**·0.75(Et₂O)·0.25(C₆H₁₄). The collected data were reduced by the program CrystalClear (Rigaku and MSC, ver. 1.3, 2001), and absorption corrections (multi-scan) were applied, which resulted in transmission factors ranging from 0.264 to 0.469 for **1**, 0.3269 to 0.6935 for **2** and 0.540 to 0.718 for **3**·0.75(Et₂O)·0.25(C₆H₁₄). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections.

The structures were solved by direct methods¹² and refined by full-matrix least-squares procedures based on $|F|^{2,13}$ When crystal $3.0.75(Et_2O).0.25(C_6H_{14})$ was separated from its mother liquor, rapid evaporation of part of the solvated molecules in the crystal was observed. Although numerous attempts were made, this crystal always weakly diffracted, especially at high angles, which made the final R value relatively higher. Therefore, one of the Et₂O and n-C₆H₁₄ molecules in $3.0.75(Et_2O).0.25(C_6H_{14})$ were refined with occupancy factors of 0.5 to give reasonable temperature factors. For 1 and 2, C(4) atoms were found to be disordered over two positions and were refined using disorder models with ratios of 0.58 : 0.42 for 1 and 0.65 : 0.35 for 2. All the non-hydrogen atoms, except the solvent molecules in $3.0.75(Et_2O).0.25(C_6H_{14})$, were refined anisotropically. The hydrogen atoms on C3, C4, C5 in 1, 2 and the solvent molecules in $3.0.75(Et_2O).0.25(C_6H_{14})$ were not located, other hydrogen atoms were placed in geometrically idealized positions (C–H = 0.981 Å for methyl groups, C-H = 0.99 Å for methylene groups and C-H =0.95 Å for phenyl groups) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.5 U_{eq}(C)$ for methyl groups and $U_{iso}(H) =$ 1.2 $U_{eq}(C)$ for methylene and phenyl groups. All the calculations were performed on a PC computer using a SHELXL-97 software package.12 Details of the intensity data collection and crystal data are given in Table 4.

Acknowledgements

Financial support from the National Nature Science Foundation of China is gratefully acknowledged.

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