

Catalytic activity of allyl-, azaallyl- and diaza-pentadienyllanthanide complexes for polymerization of methyl methacrylate[☆]

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Abstract

A variety of allylic, aza-allylic and 1,5-diazapentadienyllanthanide compounds were synthesized and their polymerization catalysis toward methyl methacrylate were examined. Divalent Sm[1,3-bis(trimethylsilyl)propenyl]₂(THF)₂ **1** and Sm(1,3-diphenylpropenyl)₂(THF)₂ **2** were synthesized by the reaction of potassium 1,3-bis(trimethylsilyl)propenide or potassium 1,3-diphenylpropenide with SmI₂. The aza-allyllanthanide compound was synthesized by the reaction of 2-pyridylbenzyl lithium with SmCl₃ followed by the reaction with LiCH(SiMe₃)₂ to give (2-pyridylbenzyl)₂SmCH(SiMe₃)₂ **3**. 1,5-Diazapentadienyllanthanide was prepared by the reaction of K[(C₅H₄N)₂CPh] with YbBr₂ to give Yb[(C₅H₄N)₂CPh]₂(THF)₂ **4**, which crystalizes monoclinic, space group C2/C (No. 15), with *a* = 35.19(1), *b* = 13.613(3), *c* = 26.552(7) Å, β = 133.77(1)°, and *Z* = 8. Preparations of divalent samarium and ytterbium complexes with bis(2-pyridylphenylmethyl)dimethylsilane ligand (**6** and **7**) were carried out by the reaction of dipotassium salt of bis(2-pyridylphenylmethyl)dimethylsilane with SmI₂ or YbBr₂. By using the resulting compounds **1**, **2**, **3**, **4**, **6** and **7** as initiator, we have examined their catalytic activities for the polymerization of methyl methacrylate and found that compounds **6** and **7** are effective to give high molecular weight isotactic polymers. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Complexes; Polymerization catalysis; Methyl methacrylate; Allyllanthanide; Azaallyllanthanide

1. Introduction

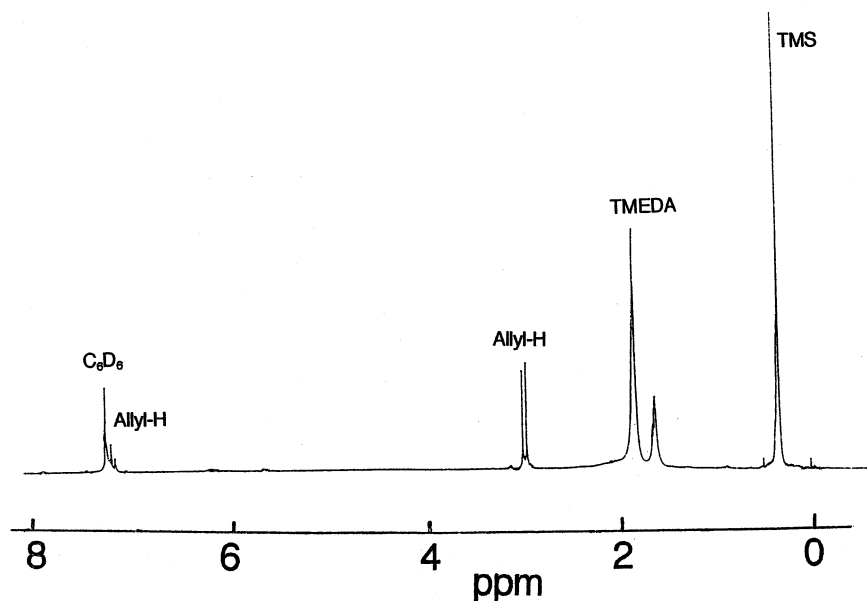
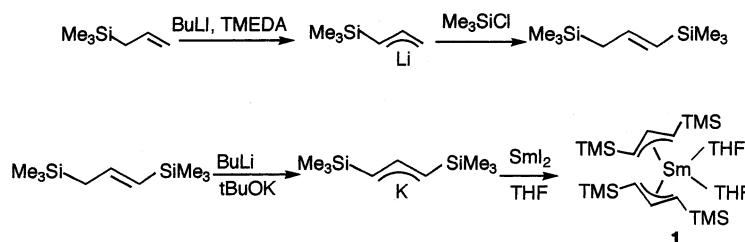
We have reported the living polymerization of alkyl methacrylates [1] and alkyl acrylates [2] by the metallocene type organic rare earth metal complexes, which produce high molecular weight polymers (*M_n* > 100 000) with very narrow molecular weight distribution (*M_w*/*M_n* < 1.05). Especially noteworthy is the highly stereospecific polymerization of methyl methacrylate (MMA) at low temperature to give 96% syndiotacticity. More recently, Novak reported high catalytic activity of metallocene type bifunctional allyl

rare earth metal complex toward MMA [3]. Although simple metallocene type allyl compounds have been synthesized, their catalytic activities have not yet been reported [4,5]. On the other hand, only a limited number of non-metallocene type rare earth metal compounds has been reported as polymerization initiator. For example, Ln(allyl)₄Li (Ln = Ce, Nd, Sm, Gd, Dy) is found to serve as initiator for the polymerization of butadiene to give *trans*-rich 1,4-poly(butadiene) [6]. Preparation of aza-allylytterbium, bis(SiMe₃N-CPhCHSiMe₃)Yb [7] and amidinate compound bis(SiMe₃N-CPh-NSiMe₃)YR, [8] has been reported but their catalytic activity was not known. This paper describes the synthesis of non-metallocene type novel bis-allyl-, bis-azaallyl- and bis-diazapentadienyllanthanide compounds and their catalytic activities for the polymerization of MMA.

[☆] Dedicated to the late Professor Rokuro Ogawara as a tribute to his memory.

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Fig. 1. ^1H -NMR spectrum of $[1,3-(\text{Me}_3\text{Si})_2\text{prpenyl}]_2\text{Sm}(\text{TMEDA})$.

Scheme 1.

2. Results and discussion

2.1. Synthesis of bis(allyl)lanthanide compound

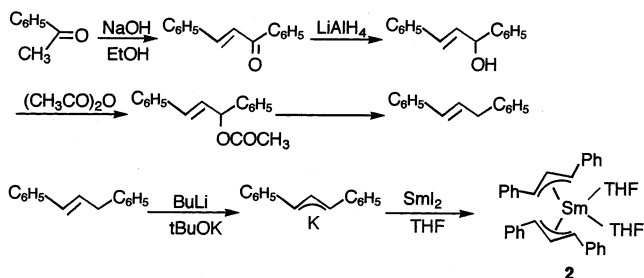
1,3-Bis(trimethylsilyl)allylsamarium compound was prepared by the reaction of 1,3-bis(trimethylsilyl)allyl potassium with SmI_2 in the presence of N,N,N',N' -tetramethylethylenediamine (TMEDA) as highly air sensitive pale-brown crystals in 36% yield. The ^1H -NMR spectrum indicates the presence of one equimolar amount of TMEDA (1.7 and 1.9 ppm) and allyl groups (d, 2.9 ppm and q, 7.2 ppm) (Fig. 1). However, the resulting compound shows only a little catalytic activity for the polymerization of MMA presumably due to the strong donation of TMEDA molecule to Sm atom. Therefore, we have examined the synthesis of corresponding THF adduct as shown in Scheme 1. The desired compound bis[1,3-bis(trimethylsilyl)propenyl] $\text{Sm}(\text{THF})_2$ **1** was obtained as a red oil in 23% yield. More pure compound $[1,3-(\text{trimethylsilyl})\text{propenyl}]_2\text{Sm}(\text{DME})_2$ was obtained as a pale-brown solid in 49% yield when 1,2-dimethoxyethane (DME) was used in place of THF but recrystallization from THF/hexane did not give crystals suitable for X-ray diffraction (^1H -NMR; SiMe_3 0.4 ppm, DME 2.7

and 2.9 ppm, allyl 3.1 and 6.9 ppm). Thus, two allyl moieties exist in the same magnetic circumstances to indicate the presence of high symmetrical structure.

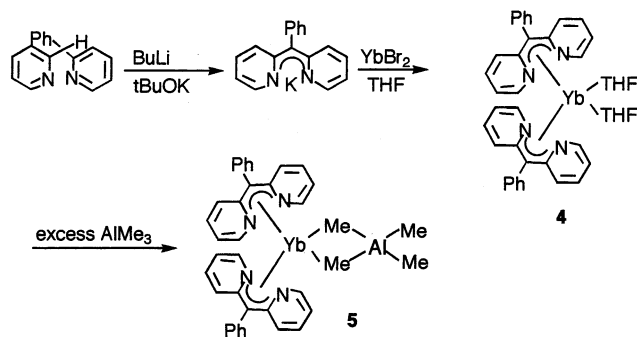
Synthesis of divalent (1,3-diphenylallyl) $_2\text{Sm}$ was explored using potassium 1,3-diphenylpropenide and SmI_2 (Scheme 2). Although ^1H -NMR spectrum (see Section 3) shows the formation of the desired compound, bis(1,3-diphenylprpenyl) $_2\text{Sm}(\text{THF})_2$ **2**, in quantitative yield, the reaction gave the product as an oily compound presumably due to their large coordinative unsaturation.

2.2. Preparation of bis(2-pyridylbenzyl) $\text{SmCH}(\text{SiMe}_3)_2$

In order to obtain crystalline allyl samarium compound, we have used the aza-allyl ligand in place of the conventional allylic ligands, because the donation of a nitrogen atom to samarium will enhance the strong bond-formation. Furthermore, trivalent complexes should lower the coordinative unsaturation. Therefore, synthesis of the trivalent aza-allylsamarium was examined here (Scheme 3). The 2:1 reaction of 2-pyridylbenzyl lithium with anhydrous SmCl_3 gave desired $(\text{C}_5\text{H}_4\text{N}-\text{CHPh})_2\text{SmCl}_2\text{Li}(\text{THF})_2$ as evidenced by the ^1H -NMR spectrum (see Section 3). Then a bulky alkyl-



Scheme 2.

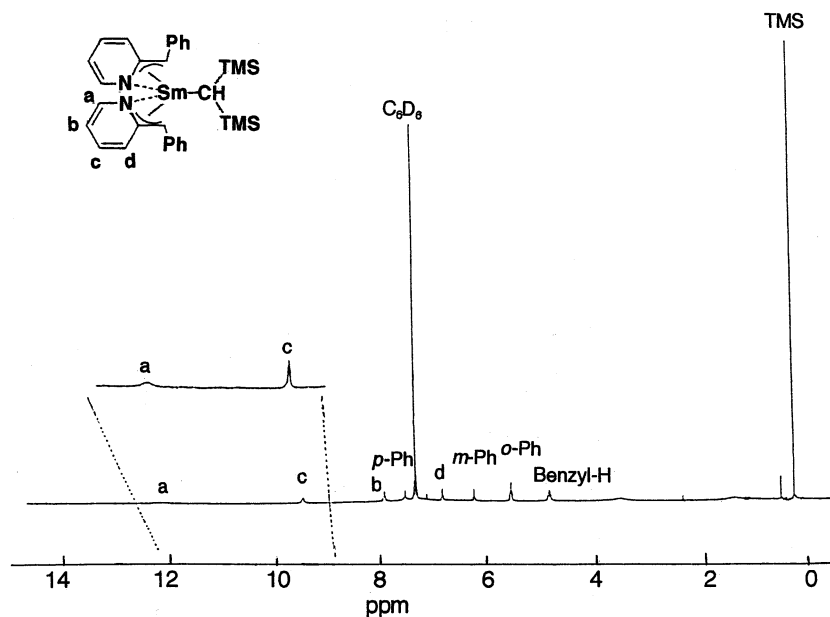


Scheme 4.

2.3. Preparation of bis[(2-pyridyl)₂CPh]Yb(THF)₂ 4

The introduction of one nitrogen atom to the allyl ligand does not successfully bring about the formation of good crystals. Therefore, we introduced two nitrogen atoms into the pentadienyl ligand at the 1- and 5-positions. The resulting compound is considered as a kind of open metallocene compound. Although the reaction of SmI_2 with $\text{K}[(\text{C}_5\text{H}_4\text{N})_2\text{CPh}]$ gave an oily compound containing some impurities, the reaction of YbBr_2 gave the desired complex, bis[(2-pyridyl)₂CPh]Yb(THF)₂ 4, as red crystals in 86% yield based on the potassium compound (Scheme 4). The structure was analyzed by $^1\text{H-NMR}$ (C_6D_6) as shown in Fig. 3. Finally the X-ray analysis was performed on this compound (ORTEP drawing is shown in Fig. 4). The crystal data and experimental conditions are summarized in Table 1, and selected bond distances and angles are given in

lithium, bis(trimethylsilyl)-methylolithium, was added to this THF solution to afford $(\text{C}_5\text{H}_4\text{N-CHPh})_2\text{SmCH}(\text{SiMe}_3)_2$ 3 in 75% yield as red crystals. Its $^1\text{H-NMR}$ spectrum is given in Fig. 2. $(\text{C}_5\text{H}_4\text{N-CHPh})_2\text{SmCl}_2\text{Li}(\text{THF})_2$ is insoluble in hexane but $(\text{C}_5\text{H}_4\text{N-CHPh})_2\text{SmCH}(\text{SiMe}_3)_2$ becomes very soluble. The molecular weight determination obtained cryoscopically in benzene agreed to their monomeric form (see Section 3). However, we have not succeeded in determining the structure of 3 by X-ray analysis.

Fig. 2. $^1\text{H-NMR}$ spectrum of $(2\text{-pyridylbenzyl})_2\text{SmCH}(\text{SiMe}_3)_2$ 3.

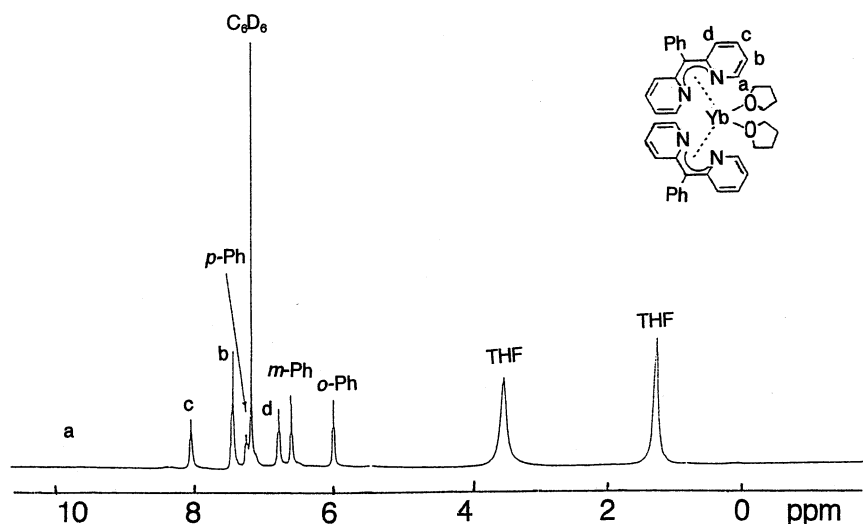
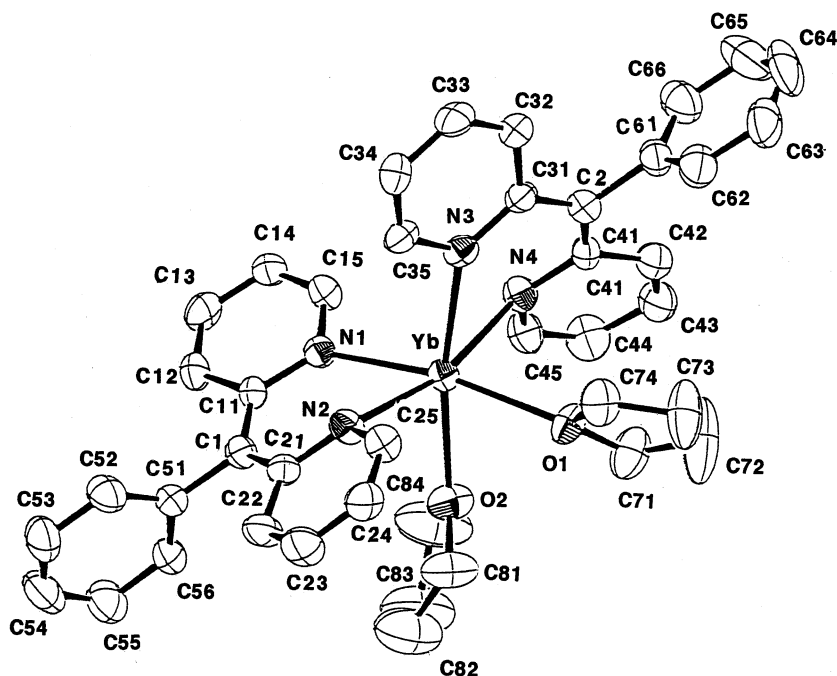
Fig. 3. ^1H -NMR spectrum of $[(2\text{-Pyr})_2\text{CPh}]_2\text{Yb}(\text{THF})_2$ 4.Fig. 4. ORTEP drawing of $[(2\text{-pyr})_2\text{CPh}]_2\text{Yb}(\text{THF})_2$ 4.

Table 2. The Yb compound is hexa-coordinated with four nitrogen atoms and two oxygen atoms. The average bond distances of the Yb–N atoms (2.436 Å) are greater than the Yb–N bonds of the divalent $\text{Yb}[\text{NR}(\text{CPh})\text{CHR}]_2$ (2.33 Å) [7]. Therefore, the Yb–N bonding in the present complex is rather loose as compared with $\text{Yb}[\text{NR}(\text{CPh})\text{CHR}]_2$. However, the Yb–N bonding between the Yb atom and the coordinated pyridine in $(\text{C}_8\text{H}_8)\text{Yb}(\text{C}_5\text{H}_5\text{N})_3$ is much greater (2.56–2.59 Å) than the present compound [9]. The Yb–O bond distances (2.456 Å) are nearly the same as that (2.41 Å) of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{THF})(\text{C}_7\text{H}_8)_{0.5}$ [10].

2.4. Preparation of $\text{bis}[(2\text{-pyridyl})_2\text{CPh}]\text{Yb}(\mu\text{Me})_2\text{AlMe}_2$ 5

Since divalent $\text{bis}[(2\text{-pyridyl})_2\text{CPh}]\text{Yb}(\text{THF})_2$ was obtained in pure form, we have examined the synthesis of corresponding trivalent complex by reacting with excess AlR_3 . In fact, the addition of excess AlMe_3 brings about the formation of $\text{bis}[(2\text{-pyridyl})_2\text{CPh}]\text{Yb}(\mu\text{Me})_2\text{AlMe}_2$ 5 in high yield (85%) as orange single crystals. The ^1H -NMR spectrum (Fig. 5) shows the single resonance of AlMe_4 group at room temperature and we could not find any coordinated solvent such as THF. The measurement of the molecular weight cryoscopically in benzene indicates that the complex

exists as monomeric form (calc. 722.8, observed 735). Addition of excess THF or ether, however, did not remove the coordinated AlMe_3 to form $\text{bis}[(2\text{-pyridyl})_2\text{CPh}]_2\text{YbMe}(\text{donor})$ and even the use of a strong donor, pyridine, is ineffective to remove the coordinated AlMe_3 . Thus, the nature of the present complex differs greatly from $\text{Cp}_2\text{Yb}(\mu\text{-Me})_2\text{AlMe}_2$ [11], $\text{Cp}_2\text{Y}(\mu\text{-Me})_2\text{AlMe}_2$ [12] and $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Me})_2\text{AlMe}_2$ [13].

2.5. Preparation of divalent samarium and ytterbium complexes with bis(2-pyridylphenylmethyl)dimethylsilane ligand (**6** and **7**)

We have synthesized also silylene bridged aza-allyl

Table 1
Crystal data and experimental factors for $[(2\text{-pyr})_2\text{CPh}]_2\text{Yb}(\text{THF})_2$ **4**

Experimental formula	$\text{YbC}_{50}\text{N}_4\text{H}_{58}\text{O}_2$
Formula weight	920.7
Crystal color	colorless
Crystal system	monoclinic
Space group	$C2/c$ (no. 15)
a (Å)	35.19(1)
b (Å)	13.613(3)
c (Å)	26.552(7)
β (°)	133.77(1)
V (Å ³)	9185(4)
Z	8
$D_{\text{calc.}}$ (g cm ⁻³)	1.331
$F(000)$	3776
μ (Mo–K α) (cm ⁻¹)	20.77
Crystal dimension	$0.3 \times 0.3 \times 0.25$
2θ range	$3 < 2\theta < 50$
Scan width 2θ	$(0.68 + 0.35 \tan \theta)^\circ$
Scan speed (° min ⁻¹)	10.0
Reflection observed	10029
Unique reflection	10018
Radiation damage	No
No. of observation ($I > 3.00\sigma(I)$)	5896
No. of variables	650
GOF	2.97
R	0.058
R_w	0.059

Table 2
Selected bond distances (Å) and bond angles (°) for complex **4**

Bond lengths (Å)			
Yb–N(1)	2.434(7)	N(1)–C(15)	1.36(1)
Yb–N(2)	2.419(8)	N(1)–C(11)	1.36(1)
Yb–N(3)	2.428(8)	C(1)–C(11)	1.41(1)
Yb–N(4)	2.425(8)	C(1)–C(21)	1.43(1)
Yb–O(1)	2.456(7)	N(2)–C(21)	1.39(1)
Yb–O(2)	2.456(8)	N(2)–C(25)	1.35(1)
Bond angles (°)			
O(1)–Yb–O(2)	78.0(2)	N(2)–Yb–N(4)	165.3(3)
N(1)–Yb–N(2)	73.4(3)	N(1)–Yb–N(4)	96.6(3)
N(3)–Yb–N(4)	73.0(3)	C(31)–C(2)–C(41)	127.7(9)
N(1)–Yb–N(3)	99.4(3)	C(11)–C(1)–C(21)	128.7(9)
N(1)–Yb–O(1)	167.9(2)		

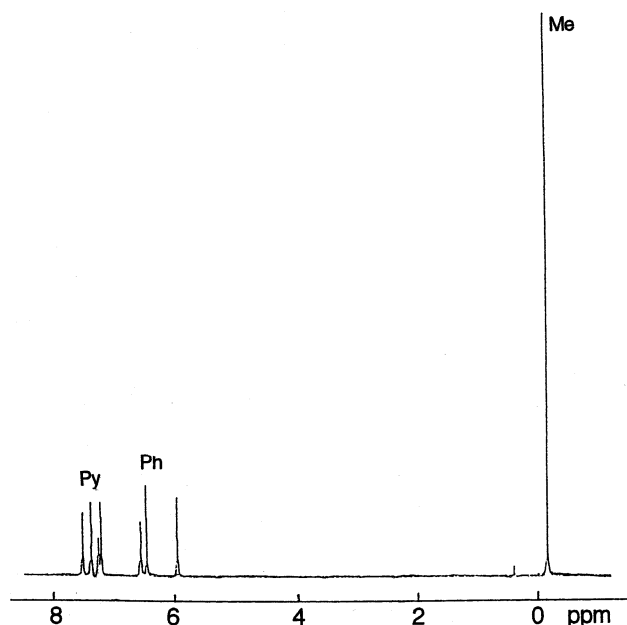
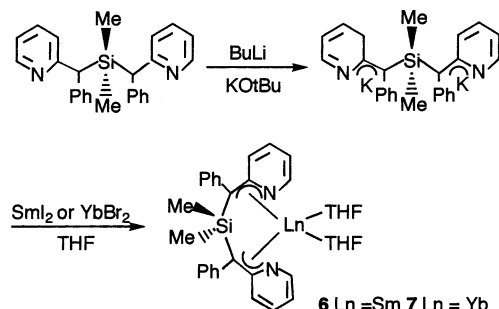


Fig. 5. ^1H -NMR spectrum of $[(2\text{-pyr})_2\text{CPh}]_2\text{Yb}(\mu\text{-Me})_2\text{AlMe}_2$ **5**.



Scheme 5.

compounds of samarium and ytterbium in 45 and 52% yields, respectively, following the Scheme 5. The ligand was prepared by the reaction of 2-benzylpyridine with butyllithium followed by Me_2SiCl_2 in 84% yield. The desired samarium **6** and ytterbium **7** compounds were prepared by the conventional method as red crystals. The structure of **6** was confirmed by ^1H -NMR spectrum (Fig. 6) and molecular weight measurement (calc. 677.8, observed 691).

2.6. Polymerization of methyl methacrylate with **1**, **2**, **3**, **4**, **6** and **7**

All the compounds synthesized here actually exhibit no catalytic activity towards the polymerization of ethylene and 1-hexene. However, these complexes serve as good initiators for the polymerization of MMA (Table 3). The allyl complexes **1** and **2** showed relatively low catalytic activity and these catalysts gave a low molecular weight polymers with rather wide molecular weight distributions. Isotacticity is also low. In contrast

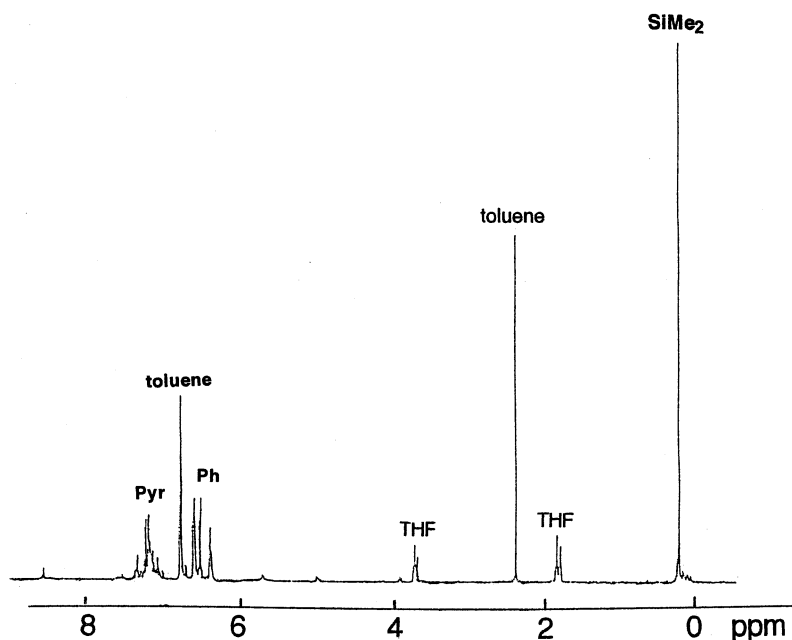


Fig. 6. ^1H -NMR spectrum of ytterbium complex with bis(2-pyridylphenylmethyl)-dimethylsilane ligand **6**.

Table 3
Polymerization of methyl methacrylate with Sm and Yb complexes

Initiator	Temperature ($^{\circ}\text{C}$)	Polymerization time (h)	Yield (%)	M_n (10^{-4})	M_w/M_n	Isotacticity (%)	Ratio (%)
1	r.t.	5	6.5	0.89	6.98	42.6	
	0	5	12.3	1.36	4.65	45.3	
2	r.t.	20	21.6	2.94	0.37	49.1	
	0	20	5.9	3.80	4.51	46.3	
3	0	3	34.1	200	3.31	64.3	
	-78	3	6.3	80.7	3.81	68.2	
4	-78	2	99.3	5.34	1.02	72.5	26.6
				2.56	1.02		73.4
6	r.t.	2	39.2	66.0	3.00	76.5	46.2
				5.51	1.57		53.8
	0	2	89.3	250	2.50	82.8	31.3
				9.56	1.43		68.7
	-78	2	72.2	256	2.55	82.3	16.4
				9.56	1.26		83.6
7	r.t.	2	46.2	155	1.87	81.9	49.8
				8.7	1.72		50.2
	0	2	81.9	255	2.01	88.5	37.2
				16.8	1.93		62.8
	-78	2	54.3	260	2.45	78.1	20.3
				18.7	2.18		79.7

to these initiators, aza-allyl lanthanide complexes showed high catalytic activities. For example, **4** gives the polymer in quantitative yield at -78°C and this initiator gives a high molecular weight poly(MMA) with a very narrow molecular weight distribution. Isotacticity is also high. Although high molecular weight monodisperse syndiotactic poly(MMA) is available by the use of the $\text{Ln}(\text{C}_5\text{Me}_5)_2\text{R}$ initiator [1], the corresponding high molecular weight isotactic polymer has not yet been obtained so far. Fig. 7 shows the plots of

M_n versus yield of polymers obtained by **4**. This result indicates the living polymerization for both high and low molecular weight polymers. Only low molecular weight isotactic poly(MMA) is available by using the RMgX initiator [14]. Therefore, the present technique is superior to other conventional catalytic systems to obtain high molecular weight isotactic polymers, although the resulting polymer shows a bi-modal pattern in GPC measurement. Catalytic activities for **6** and **7** are lower than that of **4**. The complex **4** also catalyzes the poly-

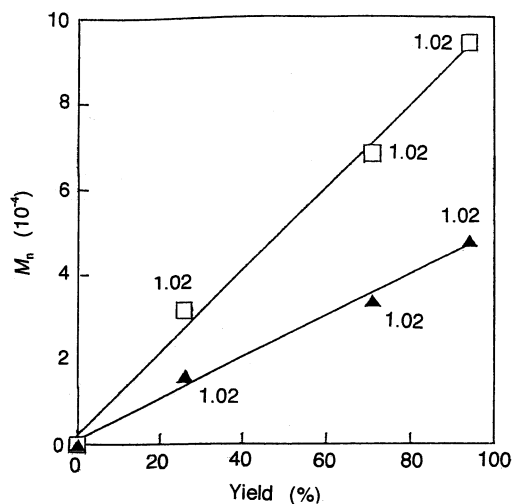


Fig. 7. Plots of M_n versus yield of polymers obtained by complex **4**, high molecular weight polymer □, low molecular weight polymer ▲.

merization of ϵ -caprolactone and hexyl isocyanate (Table 4).

3. Experimental

3.1. General

All the manipulations were carried out by using the standard Schlenk technique under an argon atmosphere. Toluene and THF were dried over calcium hydride and then over sodium benzophenone ketyl, and finally these were distilled just before use. NMR spectra were recorded on a JEOL JNM-LA400 and a Bruker AM-X400wb instruments. Chemical shifts were calibrated using benzene (7.21 ppm), chloroform (7.26 ppm) and toluene (2.09 ppm). The X-ray diffraction data were collected on a Rigaku AFC5R diffractometer using a suitable crystal sealed in a thin-walled glass capillary tube under argon. Number average molecular weights and molecular weight distributions of resulting polymers were determined by gel-permeation chromatography on a Tosoh SC-8910 high speed liquid chromatograph equipped with a differential refractometer using column TSK gel G1000, G2000, G3000 and G4000 in CHCl_3 at 40°C.

Table 4
Polymerization of other monomers using complex **4**

Monomers	Temperature (°C)	Time (h)	Yield (%)	M_n (10^{-4})	M_w/M_n
ϵ -Caprolactone	25	1	96.9	13.1	1.97
	0	1	90.9	12.6	1.85
Hexylisocyanate	0	2	34.2	36.6	3.87
	25	2	0		

3.2. Preparation of divalent 1,3-bis(trimethylsilyl)propenylsamarium compound **1**

1,3-Bis(trimethylsilyl)propene was prepared by the following procedure. 3-Trimethylsilylpropene (20 mmol, 2.93 ml) was added dropwise to a stirred mixture of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (23 mmol, 3.5 ml) and butyllithium (22.5 mmol) under argon at 5°C and the stirring was continued for 3 h. Chlorotrimethylsilane (20 mmol, 2.6 ml) was added dropwise at -5°C to this solution and the mixture was stirred for 1 h. Then the mixture was poured into HCl_{aq} (20 ml, 1 M) and extracted with hexane (100 ml). The extract was distilled to give the desired product as an oil (66–77°C/22 mmHg) in 78% yield. $^1\text{H-NMR}(\text{CDCl}_3)$ δ 6.02 (1H, dt, $-\text{CH}=\text{CH}-\text{CH}_2$), 5.42 (1H, d, $-\text{CH}=\text{CHCH}_2$), 1.62 (2H, $-\text{CH}=\text{CHCH}_2$), 0.05 (9H, s, TMS), 0.01 (9H, TMS). To a 300 ml round-bottomed flask equipped with a three way stopcock a mixture of 1,3-bis(trimethylsilyl)propene (40 mmol, 9.3 ml), KOtBu (40 mmol, 2.3 g) and THF (150 ml) was placed. Butyllithium (40 mmol) was added to this mixture and the solution was stirred for 3 h at -78°C to give potassium 1,3-bis(trimethylsilyl)propenide. On the other hand, Sm metal (10 mmol, 1.5 g), THF (80 ml) and 1,2-diiodoethane (10 mmol, 1.3 ml) was placed in 500 ml round-bottomed flask. After stirring the mixture for 3 h, potassium 1,3-bis(trimethylsilyl)propenide (30 mmol, 6.7 g) in THF solution (50 ml) was added dropwise to the THF solution (50 ml) of the resulting SmI_2 (15 mmol, 6.1 g) at room temperature. The solution was stirred overnight and evaporated to dryness. Then the residue was extracted with toluene. After the toluene was removed by vacuum distillation, the residual solid was recrystallized from hexane to give divalent $\text{Sm}[1,3\text{-bis(trimethylsilyl)propenyl}]_2(\text{THF})_2$ **1** in 23% yield (2.1 g). $^1\text{H-NMR}(\text{C}_6\text{D}_6)$ δ 6.43 (2H, $\text{CH}-\text{CH}=\text{CH}$), 3.58 (8H, bs, CH_2O of THF), 3.20 (4H, d, $\text{CH}-\text{CH}-\text{CH}$), 1.39 (8H, bs, CH_2 of THF), 0.44 (9H, s, TMS), 0.19 (9H, s, TMS), 0.03 (18H, s, TMS).

3.3. Preparation of divalent 1,3-diphenylpropenylsamarium compound **2**

Benzaldehyde (189 mmol, 20 g) was condensed with acetophenone (189 mmol, 22.6 g) in alkaline aqueous

Table 5

Final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in [(2-pyr)₂CHPh]₂Yb(THF)₂ **4**

Atom	x	y	z	B _{eq} (Å ²)
Yb	0.19206(2)	0.16479(3)	0.24112(2)	3.798(8)
O(1)	0.2104(3)	0.3244(5)	0.2974(4)	4.9(2)
O(2)	0.1034(3)	0.2351(6)	0.1679(4)	6.0(2)
N(1)	0.1549(3)	0.0194(6)	0.1673(4)	3.7(2)
N(2)	0.1874(3)	0.1995(6)	0.1476(4)	4.1(2)
N(3)	0.2839(3)	0.1158(6)	0.3283(4)	4.0(2)
N(4)	0.2069(3)	−0.0913(6)	0.3367(4)	4.2(2)
C(1)	0.1171(4)	0.0874(7)	0.0560(5)	4.0(2)
C(2)	0.3010(4)	0.1227(7)	0.4347(5)	4.3(2)
C(11)	0.1249(3)	0.0096(7)	0.0975(4)	3.7(2)
C(12)	0.1014(4)	−0.0845(8)	0.0668(6)	4.6(2)
C(13)	0.1102(4)	−0.1625(9)	0.1060(6)	5.1(3)
C(14)	0.1423(4)	−0.1508(8)	0.1771(5)	4.5(2)
C(15)	0.1624(4)	−0.0609(8)	0.2041(5)	4.4(2)
C(21)	−0.1458(4)	0.1773(7)	0.0777(5)	4.0(2)
C(22)	0.1333(5)	0.2480(8)	0.0285(6)	5.3(3)
C(23)	0.1609(5)	0.332(1)	0.0496(7)	6.2(3)
C(24)	0.2039(4)	0.3511(8)	0.1195(6)	5.2(3)
C(25)	0.2151(4)	0.2829(8)	0.1651(6)	4.4(2)
C(31)	0.3181(4)	0.1075(7)	0.4000(5)	3.8(2)
C(32)	0.3708(5)	0.0806(8)	0.4374(6)	4.6(3)
C(33)	0.3879(4)	0.0624(9)	0.4055(7)	5.0(3)
C(34)	0.3523(5)	0.0692(9)	0.3329(6)	5.3(3)
C(35)	0.3019(4)	0.0956(8)	0.2978(6)	4.5(3)
C(41)	0.2493(4)	0.1180(7)	0.4059(5)	3.6(2)
C(42)	0.2365(5)	0.1386(9)	0.4451(6)	5.3(3)
C(43)	0.1879(5)	0.1308(10)	0.4211(6)	5.8(3)
C(44)	0.1472(5)	0.098(1)	0.3518(7)	6.3(3)
C(45)	0.1593(5)	0.0812(9)	0.3152(6)	5.0(3)
C(51)	0.0745(4)	0.0708(7)	−0.0222(5)	4.3(2)
C(52)	0.0852(5)	0.049(1)	−0.0617(6)	5.9(3)
C(53)	0.0465(7)	0.035(1)	−0.1328(7)	7.4(4)
C(54)	−0.0048(6)	0.042(1)	−0.1653(7)	7.2(4)
C(55)	−0.0185(6)	0.063(1)	−0.1295(7)	6.8(4)
C(56)	0.0218(4)	0.0777(9)	0.0585(5)	5.0(3)
C(61)	0.3442(4)	0.1405(9)	0.5119(5)	5.1(3)
C(62)	0.3771(5)	0.222(1)	0.5376(7)	6.7(4)
C(63)	0.4174(6)	0.242(1)	0.609(1)	9.2(6)
C(64)	0.4240(7)	0.174(2)	0.6532(9)	11.0(6)
C(65)	0.3929(7)	0.094(2)	0.6307(8)	9.8(6)
C(66)	0.3533(6)	0.076(1)	0.5600(7)	7.2(4)
C(71)	0.1861(7)	0.359(1)	0.320(1)	7.0(5)
C(72)	0.221(1)	0.423(3)	0.376(2)	14(1)
C(73)	0.265(1)	0.441(2)	0.383(1)	9.9(6)
C(74)	0.2584(6)	0.376(1)	0.3340(8)	6.0(4)
C(81)	0.0914(6)	0.324(1)	0.1293(9)	7.6(4)
C(82)	0.035(1)	0.318(3)	0.063(2)	12.6(9)
C(83)	0.0114(9)	0.253(2)	0.079(2)	11.7(8)
C(84)	0.0567(7)	0.192(2)	0.141(2)	12.1(7)

ethanol [NaOH (237 mmol, 19.5 g), ethanol (54 ml) and water (85 ml)]. After stirring the mixture for 3 h, the solution was neutralized with HCl_{dil.} solution and then the ethanol was distilled under reduced pressure. The residue was extracted further with ether and the extract was washed with water, dried and evaporated in vacuo. Recrystallization of the solid from aqueous ethanol gave a light yellow crystals (*trans*-chalcone) (31.4 g,

yield 80%, m.p. 55.5–56°C). A solution of *trans*-chalcone (60 mmol, 12.8 g) in dry THF (25 ml) was added dropwise to an ice-cold stirred solution of LiAlH₄ (40 mmol, 1.5 g) in dry THF (75 ml) under argon and stirring was continued for 1 h at room temperature. After decomposing the mixture with 2N H₂SO₄, THF was distilled out and the product was extracted with ether (150 ml) to give 1,3-diphenylpropan-1-ol (12.1 g) in 95% yield. 1,3-Diphenylpropane-1-ol (25 mmol, 5.30 g) was refluxed with acetic anhydride (40.7 mmol, 4.1 g) in pyridine (10 ml) for 1 h, and the mixture was poured into 1N HCl solution (150 ml). The product was extracted with ether and the extract was washed with 1N HCl solution, sodium carbonate solution, and evaporated to give 1,3-diphenyl-2-propyl acetate (6.3 g) in 90% yield. 1,3-Diphenyl-2-propene was prepared by the pyrolysis of 1,3-diphenyl-2-propenyl acetate (20 mmol, 5 g) in a kugelroll. The total pyrolysis time is 30 min. Column chromatography of the crude product gave pure 1,3-diphenyl-2-propene (1.59 g) ¹H-NMR (CDCl₃) δ 7.39–7.22 (10H, aromatic, Ph × 2), 6.47 (1H, d, CH = CHCH₂), 6.38 (1H, d, CH = CHCH₂), 3.57 (2H, d, CH = CHCH₂). To a 300 ml round-bottomed flask equipped with a three way stopcock 1,3-diphenyl-2-propene (40 mmol, 9.7 ml), KOtBu (40 mmol, 2.2 g) and THF (150 ml) were placed. Butyllithium (40 mmol) was added to this solution and the mixture was stirred for 3 h at −78°C to give potassium 1,3-diphenylpropenide, which was then added dropwise to the solution of SmI₂ (20 mmol, 8.1 g) in THF (150 ml) at room temperature. After stirring the mixture overnight, THF was distilled out and the residue was extracted with toluene. Recrystallization from hexane gave bis(1,3-diphenylpropenyl)Sm(THF)₂ **2** as an orange solid in 78% yield (10.2 g). ¹H-NMR (C₆D₆) δ 7.32–7.56 (20H, m, Ph), 6.42 (4H, d, CH), 3.65 (8H, bs, THF), 3.33 (4H, d, CH), 1.45 (8H, bs, THF).

3.4. Preparation of bis(2-pyridylbenzyl)SmCH(SiMe₃)₂ **3**

To a 100 ml round-bottomed flask equipped with a three way stopcock 2-benzylpyridine (30 mmol, 4.8 ml) and THF (30 ml) were placed. Butyllithium (30 mmol) was added to this solution and the mixture was stirred for 3 h at −78–0°C to give 2-pyridylbenzyl lithium, C₅H₅NCHPhLi, in 80% yield. A THF solution of 2-pyridylbenzyl lithium (20 mmol, 3.5 g) was added to SmCl₃ (10 mmol, 2.6 g) in THF (30 ml) and the mixture was stirred overnight. After the evaporation of the solution, the residue was extracted with toluene. The toluene was evaporated and the residue was recrystallized from THF/hexane (1:1) to give bis(2-pyridylbenzyl)SmCl₂Li(THF)₂ in 57% yield (4.0 g). ¹H-NMR (CDCl₃) δ 8.72 (2H, d, 4-position of Py), 8.48 (2H, bs, 6-position of Py), 7.54 (2H, t, 5-position of Py), 7.12

(2H, d, *p*-Ph), 6.77 (2H, t, 3-position of Py), 6.39 (2H, s, CH), 5.80 (4H, t, *m*-Ph), 4.92 (4H, bs, *o*-Ph), 3.80 (8H, bs, THF), 1.48 (8H, bs, THF). Molecular weight measurement: cryoscopically in benzene, observed 756; calc. 704.89.

An ether solution of 0.56 M $\text{LiCH}(\text{SiMe}_3)_2$ (5.6 mmol) was added to a toluene solution (60 ml) of $\text{bis}(2\text{-pyridylbenzyl})\text{SmCl}_2\text{Li}(\text{THF})_2$ (5.6 mmol, 4.0 g) at 0°C and the mixture was stirred for 24 h at room temperature. After the removal of toluene, the residue was extracted with hexane (100 ml). Centrifugation followed by recrystallization from hexane gave a red powder of $\text{bis}(2\text{-pyridylbenzyl})\text{SmCH}(\text{SiMe}_3)_2$ in 75% yield (2.6 g). $^1\text{H-NMR}$ (CDCl_3) δ 12.1 (2H, bs, 6-position of Py), 9.33 (2H, d, 4-position of Py), 7.79 (2H, t, 5-position of Py), 7.40 (2H, d, *p*-Ph), 6.70 (3H, t, 3-position of Py), 6.10 (4H, t, *m*-Ph), 5.40 (4H, bs, *o*-Ph), 4.66 (2H, s, CH), 0.35 (1H, s, $\text{CH}(\text{SiMe}_3)_2$), 0.10 (9H, SiMe_3). Molecular weight measurement: observed 650; calc. 646.10.

3.5. Preparation of $\text{bis}[(2\text{-pyridyl})_2\text{CPh}] \text{Yb}(\text{THF})_2$ **4**

To a round-bottomed flask equipped with a three way stopcock 2-benzylpyridine (0.4 mol, 64.2 g) and ether (120 ml) were placed. Butyllithium (0.44 mol) was added to this solution with a dropping funnel and the mixture was stirred for 3 h at $-78-0^\circ\text{C}$ to give the aza-allyl salt. Bromopyridine (0.5 mol, 48.1 ml) was dropwise added at 0°C and the mixture was stirred overnight and then poured into excess NaHCO_3 solution, which was then extracted with ether (3×100 ml). The yellow oil thus obtained was washed with hexane and dried to yield yellow solid of dipyridylphenylmethane in 46% yield (45.2 g). $^1\text{H-NMR}$ (CDCl_3) δ 8.66 (2H, Py), 7.72 (2H, Py), 7.43–7.31 (7H, Py and Ph), 7.19 (2H, Py), 5.94 (1H, CH). To a 100 ml round-bottomed flask dipyridylphenylmethane (14 mmol, 4.0 g) and THF (50 ml) were placed. Butyllithium (14 mmol) was added to this solution and the mixture was stirred for 3 h at 0°C–room temperature to give $\text{Li}[(\text{C}_5\text{H}_4\text{N})_2\text{CPh}](\text{THF})_2$. Then KOtBu (14 mmol, 0.8 g) dissolved in THF was added and the mixture was stirred overnight. THF was removed by distillation and the residue was washed with hexane (3×30 ml) to remove LiOtBu . THF solution of potassium salt $\text{K}[(\text{C}_5\text{H}_4\text{N})_2\text{CPh}]$ (8 mmol, 2.3 g) was added dropwise to the solution of YbBr_2 (4 mmol, 1.2 g) in THF (80 ml) at 0°C. The solution was stirred at room temperature overnight and THF was removed under reduced pressure. After extracting the residue with toluene (50 ml), the solution was evaporated to dryness and the residue was recrystallized from THF/hexane (1:1) to give the ytterbium(II) complex, $[(\text{C}_5\text{H}_4\text{N})_2\text{CPh}]_2\text{Yb}(\text{THF})_2$, as dark red crystals in 86% yield (2.8 g). $^1\text{H-NMR}$ (CDCl_3) δ 9.65 (4H, bs, 6-posi-

tion of Py), 8.11 (4H, bs, 4-position of Py), 7.49 (4H, bs, 5-position of Py), 7.28 (2H, bs, *p*-Ph), 6.82 (4H, 3-position of Py), 6.63 (4H, d, *m*-Ph), 6.03 (4H, *o*-Ph), 3.38 (8H, bs, THF), 1.21 (8H, bs, THF).

3.6. Preparation of $\text{bis}[(2\text{-pyridyl})_2\text{CPh}] \text{Yb}(\mu\text{-Me})_2 \text{AlMe}_2$ **5**

To a stirred solution of the ytterbium(II) species $[(\text{C}_4\text{H}_4\text{N})_2\text{CPh}]_2\text{Yb}(\text{THF})_2$ (5 mmol, 4.0 g) in 100 ml toluene, five equivalents of AlMe_3 (25 mmol, 2.3 ml) were added. During stirring the mixture for 24 h, orange precipitates were generated in an orange solution. Then the mixture was washed with 200 ml of hexane to separate the resulting $[(2\text{-pyridyl})_2\text{CPh}]_2\text{Yb}(\mu\text{-Me})_2\text{AlMe}_2$ from AlMe_3 . The residue was dissolved into toluene (100 ml). Centrifugation followed by recrystallization from hexane/toluene gave orange crystals of $[(2\text{-pyridyl})_2\text{CPh}]_2\text{Yb}(\mu\text{-Me})_2\text{AlMe}_2$ in 85% yield (3.1 g). $^1\text{H-NMR}$ (CDCl_3) δ 7.47 (4H, d, 6-position of Py), 7.33 (4H, t, 4-position of Py), 7.21 (2H, t, *p*-Ph), 7.17 (4H, d, 5-position of Py), 6.48 (4H, t, 3-position), 6.37 (4H, d, *m*-Ph), 5.87 (4H, t, *o*-Ph), -0.20 (12H, s, Me).

3.7. Preparation of divalent samarium and ytterbium complexes with the $\text{bis}(2\text{-pyridylphenylmethyl})\text{-dimethylsilane}$ ligand (**6** and **7**)

To a 500 ml round-bottomed flask equipped with a three way stopcock 2-benzylpyridine (0.2 mol, 32.1 g) and THF (200 ml) were placed. Butyllithium (0.2 mol) was added to this solution at 0°C and the mixture was stirred for 3 h to give the aza-allyllithium salt. Dichlorodimethylsilane (0.1 mol, 12.1 ml) was added dropwise to this solution and the mixture was stirred for 5 h. The reaction mixture was poured into NaHCO_3 aqueous solution, which was then extracted with ether (100 ml). The extract was washed with methanol to yield a white solid of $\text{bis}(2\text{-pyridylphenylmethyl})\text{dimethylsilane}$ in 84% yield (33.1 g). $^1\text{H-NMR}$ (CDCl_3) δ 8.66 (2H, m, Py), 7.72 (2H, m, Py), 7.43–7.31 (7H, m, Py and Ph), 7.19 (2H, Py), 5.94 (1H, CH) 0.05 (CH, SiMe). Butyllithium (20 mmol) was added dropwise to a THF solution (50 ml) of $\text{bis}(2\text{-pyridylphenylmethyl})\text{dimethylsilane}$ (10 mmol, 3.9 g) and the solution was stirred for 3 h at $-78-0^\circ\text{C}$ to give the lithium salt of $\text{bis}(2\text{-pyridylphenylmethyl})\text{dimethylsilane}$. Then KOtBu (20 mmol) in THF was added at 30°C under reduced pressure and the residue was washed with hexane to remove LiOtBu . The THF solution of the dipotassium salt of $\text{bis}(2\text{-pyridylphenylmethyl})\text{dimethylsilane}$ (8 mmol, 3.7 g) was added to the solution of SmI_2 (8 mmol, 32.4 g) in THF (100 ml) at -78°C and the mixture was stirred overnight. THF was removed by distillation and the

residue was extracted with toluene (120 ml). The toluene soluble part was recrystallized from THF/hexane (1:1) to give $[(\text{Py}-\text{CPh})_2\text{SiMe}_2]\text{SM}(\text{THF})_2$ **6** as red crystals in 45% yield (4.2 g). In the case of the ytterbium complex **7**, YbBr_2 was used instead of SmI_2 .

3.8. Typical procedure for the polymerization of methyl methacrylate

Monomer (typically 100–200 equivalents to initiator) was injected via a syringe into a solution of an initiator (typically 0.04 mmol) in toluene (10 ml) with vigorous stirring at the fixed temperature (-78°C –room temperature). After stirring for a fixed time (2–20 h), the reaction mixture was poured into excess MeOH in order to quench the living polymer end. The precipitated polymer was collected and dried under vacuum. Measurement of tacticity for poly(MMA) was performed by 270 MHz ^1H -NMR in CDCl_3 (Me peak; mm 1.43, mr 1.28, rr 1.14 ppm) [15] or by 62.9 MHz ^{13}C -NMR in CDCl_3 (mmmm 176.2, mmmr 176.1, rrrr 177.9, mrrrr 177.6 ppm) [16]. The isotacticity, 88.7%, (mm%) observed corresponds to a 72% mmmm value.

3.9. X-ray structure analysis of $\text{bis}[(2\text{-pyridyl})_2\text{CPh}]\text{Yb}(\text{THF})_2$ **4**

The integrated intensity data were measured on a Rigaku AFC5R diffractometer with graphite-monochromated $\text{Mo}-\text{K}_\alpha$ ($\lambda = 0.7106 \text{ \AA}$) radiation. As the complex **4** is very air-sensitive, the crystal was sealed in a thin-walled glass capillary tube under argon atmosphere. The X-ray data were collected at room temperature using ω – 2θ scan technique to a maximum 2θ value of 50° . The data were corrected for conventional absorption, Lorentz and polarization effects. The crystal structure was solved by the heavy-atom method. Yb was found in Patterson map. Successive Fourier synthesis clearly revealed the remaining non hydrogen atoms. The non-hydrogen atoms were refined an-

isotropically by the full-matrix least-squares method, while the hydrogen atoms were fixed at their standard geometries and were not refined. All the calculations were performed using the teXsan crystallographic software package.² The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms for complex **4** are listed in Table 5.

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² teXsan: crystal structure analysis package, Molecular Structure Corporation (1985 and 1992).