



Rare earth metal benzyl complexes bearing bridged-indenyl ligand for highly active polymerization of methyl methacrylate

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ABSTRACT

The novel anionic bridged-indenyl rare earth metal benzyl complexes $[(C_9H_6SiMe_2(CH_2)_2SiMe_2C_9H_6)Ln(CH_2C_6H_4-p-tBu)_2][Li(THF)_4]$ ($Ln = Y$ (**1**), Lu (**2**)) were synthesized by an acid–base reaction of $C_9H_7SiMe_2(CH_2)_2SiMe_2C_9H_7$ with one equiv. of rare earth metal trisbenzyl complexes, which were formed *in situ* from the reaction of anhydrous $LnCl_3$ with $LiCH_2C_6H_4-p-tBu$ in 1:3 molar ratio in THF. The complexes were characterized by elemental analysis, NMR spectroscopy, FT-IR spectroscopy, and X-ray structural analysis in the case of **2**. Both complexes are active for the polymerization of methyl methacrylate (MMA) to afford high molecular weight and narrow molecular weight distribution PMMA. The molecular weights of PMMA could be controlled using **1** as a polymerization initiator in chlorobenzene at $-40^\circ C$.

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1. Introduction

Organo rare earth metal complexes have witnessed rapid progress during the past two decades, and have played promising role in the polymerization of both nonpolar and polar monomers [1–4]. In the 1990s, Yasuda and coworkers first reported that organo rare earth metal derivatives, $(C_5Me_5)_2LnR$ ($R = \text{alkyl}, H$), could serve as effective single-component catalysts for methyl methacrylate (MMA) polymerization, giving highly syndiotactic poly(MMA) in a living polymerization manner [5,6]. Since then, various kinds of rare earth metal complexes containing $Ln-C$, $Ln-N$, or $Ln-H$ σ -bonds have been investigated for MMA polymerization [7–10]. Very recently, it was found that anionic rare earth metal complexes could exhibit much higher activity than the corresponding neutral ones in the polymerization of MMA [11–15]. However, the reported anionic rare earth metal complexes showed poor ability to control polymer molecular weights. On the other hand, while a large spectrum of rare earth metal complexes with different electronic and steric configurations have been well documented, the bridged-indenyl-ligated rare earth metal complexes are relatively limited [16–27]. Herein, we would like to report the novel anionic bridged-indenyl rare earth metal benzyl complexes, as well as their extremely high activity for the polymerization of methyl methacrylate with molecular weights controllable under certain conditions.

2. Results and discussion

2.1. Synthesis and characterization of the ligand

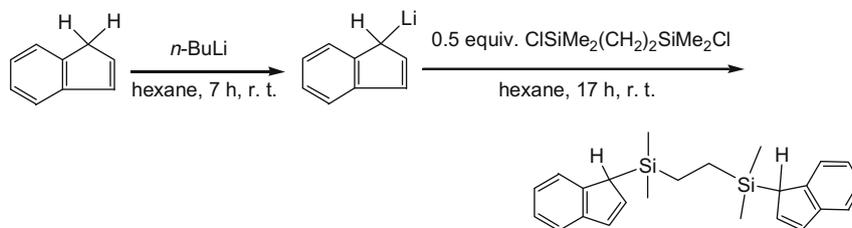
The bridged-indenyl ancillary ligand $C_9H_7SiMe_2(CH_2)_2SiMe_2C_9H_7$ was synthesized by the reaction of freshly prepared indenyl lithium (C_9H_7Li) with 0.5 equiv. of 1,2-bis(chlorodimethylsilyl)ethane in hexane at room temperature, as shown in Scheme 1. After workup, $C_9H_7SiMe_2(CH_2)_2SiMe_2C_9H_7$ was obtained as white powder in 96% isolated yield. It was characterized by NMR spectroscopy, elemental analysis, and FT-IR spectroscopy. 1H and ^{13}C NMR spectra confirmed that two indenenes were connected by 1,4-disilabutylene group through two sp^3 -hybridized carbons in each five-membered ring.

2.2. Synthesis and characterization of

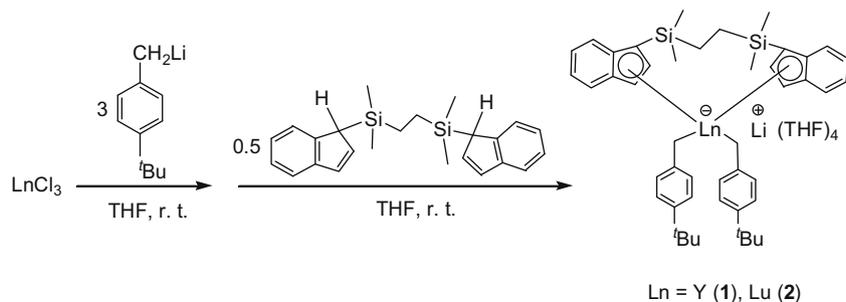
$[(C_9H_6SiMe_2(CH_2)_2SiMe_2C_9H_6)Ln(CH_2C_6H_4-p-tBu)_2][Li(THF)_4]$ ($Ln = Y$ (**1**), Lu (**2**))

Treatment of $C_9H_7SiMe_2(CH_2)_2SiMe_2C_9H_7$ with 1 equiv. of rare earth metal trisbenzyl complexes, which were formed *in situ* from the reaction of $LnCl_3$ with $LiCH_2C_6H_4-p-tBu$ in 1:3 molar ratio in THF, afforded the bridged-indenyl rare earth metal benzyl complexes $[(C_9H_6SiMe_2(CH_2)_2SiMe_2C_9H_6)Ln(CH_2C_6H_4-p-tBu)_2][Li(THF)_4]$ ($Ln = Y$ (**1**), Lu (**2**)) as pale yellow crystals in 53–59% isolated yields (Scheme 2). Both complexes were characterized by elemental analysis, FT-IR spectroscopy, and NMR spectroscopy. Single crystal structural determination of **2** revealed that it is an anionic complex.

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Scheme 1.



Scheme 2.

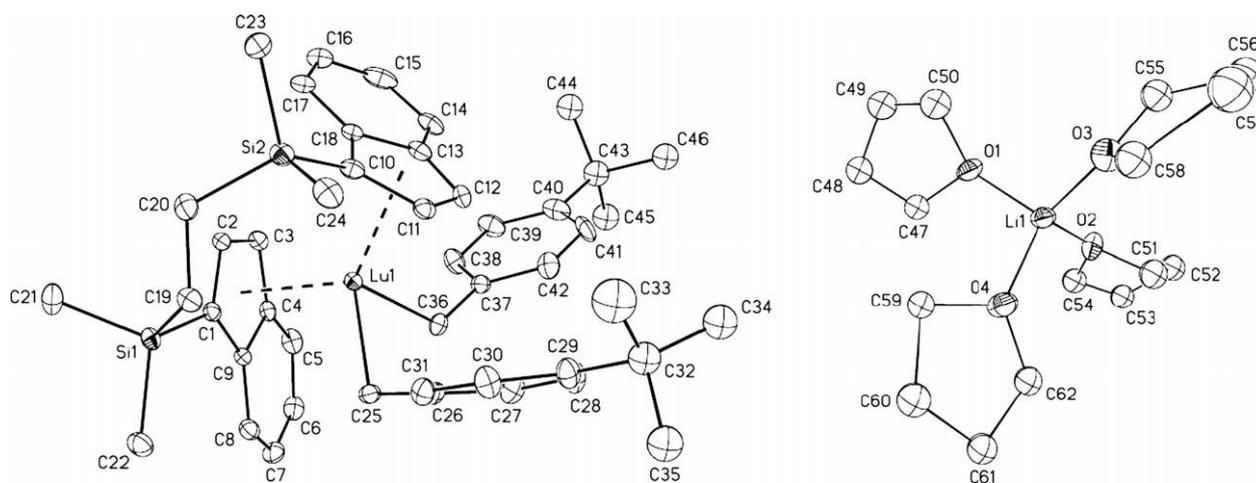


Fig. 1. Molecular structure of **2** (10% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angle (°): Lu(1)–C(1) 2.662(7), Lu(1)–C(2) 2.627(8), Lu(1)–C(3) 2.679(8), Lu(1)–C(4) 2.827(7), Lu(1)–C(9) 2.772(7), Lu(1)–C(10) 2.732(8), Lu(1)–C(11) 2.626(8), Lu(1)–C(12) 2.601(8), Lu(1)–C(13) 2.690(8), Lu(1)–C(18) 2.772(8), Lu(1)–C(25) 2.406(8), Lu(1)–C(36) 2.391(8); C(36)–Lu(1)–C(25) 89.1(3).

Both **1** and **2** are sensitive to air and moisture. However, no decomposition was observed when they were kept in the glove box at ambient temperature for couple of weeks. They are quite soluble in THF and chlorobenzene, sparsely soluble in toluene, but insoluble in aliphatic hydrocarbon solvents, such as hexane and pentane.

Single crystals of **2** suitable for X-ray diffraction were grown from a mixture solution of THF/toluene in ca. 1:2 volume ratio at $-30\text{ }^{\circ}\text{C}$. Its molecular structure, with the selected bond lengths and angles, is shown in Fig. 1. X-ray structural analysis revealed that **2** exists as crystallographically independent cation $[\text{Li}(\text{THF})_4]^+$ and anionic pair $[\{\text{C}_9\text{H}_6\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_6\}\text{Lu}(\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-}^i\text{Bu})_2]^-$ in the unit cell. The central metal Lu^{3+} is coordinated by two five-membered rings (Cp ring) of indenyl ligands and two methylene carbons of benzyl groups. The coordination geometry around the Lu^{3+} can be described as a distorted tetrahedron if the two indenyl rings, C25, and C36 are regarded as occupying an independent polyhedral vertex. The Lu–C(indenyl) bond distances range from 2.627(8) to 2.827(7) Å (C1C2C3C4C9) and 2.601(8) to 2.772(8) Å (C10C11C12C13C18). Con-

sidering the $\Delta_{\text{Lu-C(indenyl)}}$ defined as the difference of the longest and the shortest bond distances between the lanthanide ion and the indenyl ligand, the $\Delta_{\text{Lu-C(indenyl)}}$ values are 0.17 and 0.20 Å for the two indenyl groups, suggesting the bonding mode of the metal ion with indenyl ligands being partially slipped toward η^3 - from η^5 -mode, as found in *rac*- $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_9\text{H}_6)_2]\text{YbN}(\text{SiMe}_3)_2$ [23], and *meso*- $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_9\text{H}_6)_2]\text{Yb}(\text{DME})$ [24]. Taking into consideration of effective ionic radius [28], the bond distances of Lu–C(benzyl) (2.406(8) and 2.391(8) Å) are comparable with those in rare earth metal bis(benzyl) complexes, such as $[\text{PhC}(\text{N}-2,6\text{-}^i\text{Pr}-\text{C}_6\text{H}_3)_2]\text{La}(\text{CH}_2\text{Ph})_2(\text{THF})$ (2.590(5)–2.632(3) Å) [29], $[\text{Me}_2\text{TACNSiMe}_2\text{N}^i\text{Bu}]\text{La}(\text{CH}_2\text{Ph})_2$ (2.687(4)–2.699(4) Å) and $[\text{BuC}(\text{N}-2,6\text{-}^i\text{Pr}-\text{C}_6\text{H}_3)_2]\text{La}(\text{CH}_2\text{Ph})_2(\text{THF})$ (2.595(3)–2.585(3) Å) [30].

2.3. Polymerization of MMA

To investigate the reactivity of **1** and **2**, they were employed as initiators for the polymerization of MMA under various conditions. The results are summarized in Table 1. The complexes showed

much higher activity for MMA polymerization than the other bridged-indenyl rare earth metal complexes [23,24], and the activity reached up to 48,000 mol of MMA/(mol Ln·h), which can compete for the most active anionic rare earth metal complexes for MMA polymerization reported to date [11–15]. The central metal has a great influence on the activity. For example, the conversion reached 100% in 1 min in the loading of $[M]/[Ln] = 1000$ at $-40\text{ }^{\circ}\text{C}$ using **1** as the initiator, while the conversion was only 9% for **2** even the polymerization was prolonged to 30 min (Entries 3 and 4, Table 1). This activity order, as observed in other lanthanidocene initiation systems for MMA polymerization [6], may be contributed to that the ionic radii of Y (0.900 Å) is larger than of Lu (0.861 Å) [28]. Although the polymerization could proceed at a wide range of polymerization temperature (from -78 to $35\text{ }^{\circ}\text{C}$), the polymerization activity was strongly dependent on the polymerization temperature. For example, when the polymerization temperature was raised from -40 to $0\text{ }^{\circ}\text{C}$, the conversion of monomer to polymer ranged from 100% to 56% in the case of the polymerization was terminated in one minute. However, when the temperature was performed at $35\text{ }^{\circ}\text{C}$, the yield of polymer was only 40% even the polymerization was prolonged to 1 h (Entry 4, 8 and 9). This may be ascribed to that the nucleophilic substitution of carbonyl group of MMA by the benzyl group is prohibited at lower temperature [31]. As expected, the polymerization activity decreased dramatically as the polymerization was performed in polar solvent, such as THF [32].

The polymers obtained with **1** and **2** have high molecular weights ($M_n > 10^4$) and relatively narrow molecular weight distributions. In all cases, GPC curves showed a unimodal pattern, indicative of single-site catalyst behavior. It is noteworthy that, albeit with relatively low initiating efficiency (ca. 27% based on the assumption of both Ln–C(benzyl) bonds being active in the polymerization), employing **1** as the initiator in chlorobenzene at $-40\text{ }^{\circ}\text{C}$, the molecular weights of the resulting polymers increased almost linearly as the increase of the molar ratio of monomer-to-initiator, (Entries 4, and 10–12, see also Fig. 2), demonstrating

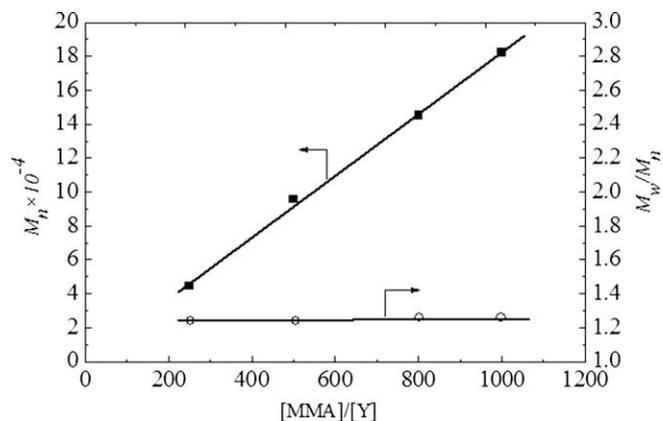


Fig. 2. M_n and M_w/M_n vs $[MMA]/[Y]$ plots for MMA polymerization using **1** as an initiator in chlorobenzene at $-40\text{ }^{\circ}\text{C}$.

the molecular weights controllable. However, different to the polymerization carried out in chlorobenzene, in which **1** has good solubility, the polymerization performed in toluene or in bulk afforded polymers with relatively broad molecular weight distribution (Entries 5–7), partially owing to the heterogeneous polymerization.

Triad microstructural analysis of the resulting polymers was carried out using ^1H NMR in CDCl_3 according to the literature [33]. The present initiation system showed poor control of stereoregularity in the polymerization, and yielded atactic PMMA.

3. Conclusions

In summary, the novel anionic bridged-indenyl rare earth metal benzyl complexes $[(\text{C}_9\text{H}_6\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_6)_2\text{Ln}(\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-}^t\text{Bu})_2][\text{Li}(\text{THF})_4]$ ($\text{Ln} = \text{Y}$ (**1**), Lu (**2**)) have been successfully synthesized by an acid–base reaction of rare earth metal trisbenzyl complexes with one equiv. of $\text{C}_9\text{H}_7\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_7$ in THF

Table 1
Polymerization of MMA Initiated by Bridged-Indenyl Rare Earth Metal Benzyl Complexes **1** and **2**.^a

Entry	Ln	[M]/[Ln]	Solvent	Temperature ($^{\circ}\text{C}$)	Time (min)	Conv ^b %	TOF ^c	M_n , calc. ^d $\times 10^{-4}$	M_n , obsd ^e $\times 10^{-4}$	M_w/M_n ^e	Tacticity (%) ^f		
											mm	rm	rr
1	Lu	500	THF	35	180	34	57	0.85	2.10	1.43			
2	Y	500	THF	35	180	38	63	0.95	1.75	1.79			
3	Lu	1000	chlorobenzene	-40	30	9	180	0.45	7.34	1.42	28.8	30.9	40.3
4	Y	1000	chlorobenzene	-40	1	100	60,000	5.01	18.23	1.27	30.0	31.5	38.5
5	Y	500	chlorobenzene	35	180	63	105	1.58	7.01	1.37	18.8	31.7	49.5
6	Y	500	toluene	35	180	69	115	1.73	5.50	2.05			
7	Y	500	35	180	78	130	1.95	7.35	2.15				
8	Y	1000	chlorobenzene	35	60	40	400	2.01	8.38	1.28			
9	Y	1000	chlorobenzene	0	1	56	33,600	2.80	11.64	1.29	26.4	29.6	44.0
10	Y	250	chlorobenzene	-40	1	100	15,000	1.25	4.45	1.24			
11	Y	500	chlorobenzene	-40	1	100	30,000	2.50	9.58	1.24			
12	Y	800	chlorobenzene	-40	1	100	48,000	4.00	14.53	1.26			
13	Y	1000	chlorobenzene	-78	1	63	37,800	3.15	12.79	1.37	32.7	31.3	36.0

^a Polymerization conditions: $\text{Ln} = 9\text{ }\mu\text{mol}$, $V_{\text{solvent}} = 1\text{ mL}$.

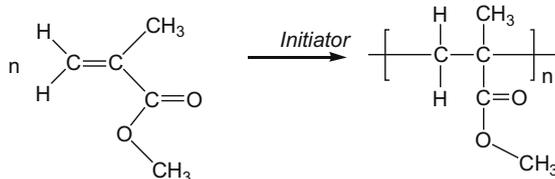
^b Conversion = weight of polymer obtained/weight of monomer used.

^c TOF = mol of MMA (mol of Ln) $^{-1}\text{h}^{-1}$.

^d $M_{\text{cal}} = ([MMA]/(2[Ln])) \times 100.12 \times \text{conversion}$.

^e Measured by GPC relative to PMMA standards.

^f Determined by ^1H NMR in CDCl_3 at $25\text{ }^{\circ}\text{C}$.



at room temperature. Both complexes can serve as single-component initiator for the polymerization of MMA at a wide range of polymerization temperature (from -40 to 35 °C), and **1** showed much higher activity than **2**. The polymerization carried out at -40 °C gave PMMA with high molecular weight ($M_n > 10^4$) and relatively narrow molecular weight distribution ($M_w/M_n < 1.42$). When the polymerization was initiated by **1** in chlorobenzene at -40 °C, the molecular weights of the resulting polymers increased almost linearly as the monomer-to-initiator ratio was increased, while the narrow molecular weight distributions remained quite narrow ($M_w/M_n = 1.24$ – 1.27), suggesting the molecular weights controllable.

4. Experimental

4.1. Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and glove box. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glove box. Chlorobenzene and MMA were dried by CaH_2 , and distilled before polymerization. Anhydrous LnCl_3 were purchased from STREM. 1-*tert*-Butyl-4-methylbenzene, *n*-BuLi (1.6 M solution in hexane), and 1,2-bis(chlorodimethylsilyl)ethane were purchased from Alfa, and used as received. Deuterated solvents (THF- d_8 , Benzene- d_6 , and CDCl_3) were obtained from CIL. $\text{LiCH}_2\text{C}_6\text{H}_4$ -*p*- t Bu was prepared according to the literature [34].

Samples of organo rare earth metal complexes for NMR spectroscopic measurements were prepared in the glove box using J. Young valve NMR tubes. NMR (^1H , ^{13}C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 °C. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations. X-ray structural determination was carried out on a Rigaku Mercury diffractometer. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 at 40 °C using THF as eluent against PMMA standards.

4.2. Synthesis of $\text{C}_9\text{H}_7\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_7$

To a hexane solution (90 mL) of freshly distilled indene (11.6 g, 100 mmol), *n*-BuLi (1.6 M, 62.5 mL, 100 mmol) in hexane solution was added slowly at room temperature. After the reaction mixture was stirred at room temperature for 7 h, 1,2-bis(chlorodimethylsilyl)ethane (10.7 g, 50.0 mmol) in 25 mL of hexane was added drop wise at room temperature. The resulting reaction mixture was stirred for 17 h to give a white slurry. Then, the white precipitate was filtered off, and the clear filtrate was dried in vacuum to afford the title product as white powder (17.9 g, 96%). ^1H NMR (C_6D_6 , 400 MHz) δ : -0.05 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.01 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.40 (m, 4H, CH_2CH_2), 3.54 (s, 2H, CH in five-membered ring), 6.63 , 7.01 , 7.34 , 7.38 , 7.56 , 7.61 (12H, Ar-H). ^{13}C NMR (C_6D_6 , 100 MHz) δ : -5.0 , -4.6 ($\text{Si}(\text{CH}_3)_2$), 7.1 (CH_2CH_2), 45.4 (CH in five-membered ring), 121.5 , 122.9 , 124.1 , 125.3 , 129.3 , 135.6 , 144.6 , 145.7 (Ar-C). FT-IR (KBr pellets, cm^{-1}): 3065 (m), 2958 (m), 2905 (m), 1449 (m), 1409 (m), 1361 (m), 1242 (s), 1134 (m), 1056 (s), 1010 (s), 814 (s), 772 (s). Anal. Calc. for $\text{C}_{24}\text{H}_{30}\text{Si}_2$: C, 76.94; H, 8.07. Found: C, 76.76; H, 8.16.

4.3. Synthesis of $[(\text{C}_9\text{H}_6\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_6)]\text{Y}(\text{CH}_2\text{C}_6\text{H}_4$ -*p*- t Bu) $_2][\text{Li}(\text{THF})_4]$ (**1**)

To a THF slurry of YCl_3 (0.39 g, 2.0 mmol), $\text{LiCH}_2\text{C}_6\text{H}_4$ -*p*- t Bu (0.93 g, 6 mmol) in 30 mL of THF was added drop wise at room

temperature. After the reaction mixture was stirred at room temperature for 3 h, $\text{C}_9\text{H}_7\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_7$ (0.37 g, 1.0 mmol) in 20 mL of THF was added slowly. After the reaction mixture was stirred for 2 hours at room temperature, the volatiles were removed in vacuum. Then the yellow residue was extracted with toluene to remove LiCl by centrifugation. The extract was dried under reduced pressure, and the resulting residue was dissolved in a mixture solution of toluene/THF in 2:1 volume ratio. Cooling to -30 °C for several days gave yellow crystals in two crops (0.56 g, 53% based on ligand). ^1H NMR ($\text{C}_6\text{D}_6/\text{THF-}d_8$, 400 MHz): δ 0.53 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.74 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 1.33 (m, 4H, CH_2CH_2), 1.52 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.56 (m, 16H, THF- β - CH_2), 2.21 (s, 4H, Ar CH_2), 3.65 (m, 16H, THF- α - CH_2), 6.03 (d, 2H, Ar-H), 6.65 (d, 2H, Ar-H), 7.02–7.26 (m, 10H, Ar-H), 7.47 (d, 2H, Ar-H), 8.08 (d, 2H, Ar-H). ^{13}C NMR ($\text{C}_6\text{D}_6/\text{THF-}d_8$, 100 MHz): δ -0.6 , -0.2 ($\text{Si}(\text{CH}_3)_2$), 9.4 (CH_2CH_2), 25.5 (THF- β - CH_2), 31.9 ($\text{C}(\text{CH}_3)_3$), 33.7 ($\text{C}(\text{CH}_3)_3$), 49.9, 50.3 (Ar CH_2), 67.5 (THF- α - CH_2), 101.6, 104.2, 118.9, 119.1, 123.5, 124.0, 124.4, 124.9, 128.5, 130.3, 132.6, 136.6, 154.4 (aromatic-C). FT-IR (KBr pellets, cm^{-1}): 3064 (m), 2962 (s), 2871 (m), 1601 (w), 1515 (w), 1458 (m), 1407 (w), 1362 (w), 1248 (m), 1132 (m), 1047 (s), 816 (s). Anal. Calc. for $\text{C}_{62}\text{H}_{90}\text{LiO}_4\text{Si}_2\text{Y}$: C, 70.81; H, 8.64. Found: C, 70.78; H, 8.27.

4.4. Synthesis of $[(\text{C}_9\text{H}_6\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_6)]\text{Lu}(\text{CH}_2\text{C}_6\text{H}_4$ -*p*- t Bu) $_2][\text{Li}(\text{THF})_4]$ (**2**)

The synthesis of **2** was carried out in the similar way as that for **1**, using LuCl_3 (1.12 g, 1.0 mmol), $\text{LiCH}_2\text{C}_6\text{H}_4$ -*p*- t Bu (0.47 g, 3.0 mmol), and $\text{C}_9\text{H}_7\text{SiMe}_2(\text{CH}_2)_2\text{SiMe}_2\text{C}_9\text{H}_7$ (0.18 g, 0.5 mmol). Complex **2** was isolated as yellow crystals in two crops (0.34 g, 59% based on ligand). ^1H NMR ($\text{C}_6\text{D}_6/\text{THF-}d_8$, 400 MHz): δ 0.15 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 0.44 (s, 6H, $\text{Si}(\text{CH}_3)_2$), 1.09 (m, 4H, CH_2CH_2), 1.21 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.36 (m, 16H, THF- β - CH_2), 2.01 (s, 4H, Ar CH_2), 3.38 (m, 16H, THF- α - CH_2), 5.55 (d, 2H, Ar-H), 6.25 (d, 2H, Ar-H), 6.64 (d, 4H, Ar-H), 6.77 (t, 2H, Ar-H), 6.85 (m, 4H, Ar-H), 6.92 (d, 4H, Ar-H), 7.10 (d, 2H, Ar-H), 7.74 (d, 2H, Ar-H). ^{13}C NMR ($\text{C}_6\text{D}_6/\text{THF-}d_8$, 100 MHz): δ -0.3 , 0.0 ($\text{Si}(\text{CH}_3)_2$), 9.6 (CH_2CH_2), 25.8 (THF- β - CH_2), 32.1 ($\text{C}(\text{CH}_3)_3$), 33.8 ($\text{C}(\text{CH}_3)_3$), 53.8 (Ar CH_2), 67.8 (THF- α - CH_2), 100.5, 102.9, 118.9, 119.4, 123.8, 124.6, 124.7, 124.9, 128.3, 128.5, 129.2, 130.4, 132.9, 137.3, 155.1 (aromatic-C). FT-IR (KBr pellets, cm^{-1}): 2961 (s), 2903 (m), 2872 (m), 1601 (w), 1515 (w), 1458 (m), 1407 (w), 1362 (w), 1248 (m), 1132 (m), 1047 (s), 816 (s). Anal. Calc. for $\text{C}_{62}\text{H}_{90}\text{LiLuO}_4\text{Si}_2$: C, 65.45; H, 7.99. Found: C, 65.36; H, 7.85.

4.5. Polymerization of MMA

All polymerization were carried out in a 50 mL Schlenk flask under Ar atmosphere. A typical polymerization reaction for MMA is given below (Entry 1, Table 1). A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged with **1** (10 mg, 9 μmol) and THF (1.0 mL). The flask was kept at 35 °C for 10 min, and then MMA (0.45 mmol) was added by a syringe. The contents in the flask were vigorously stirred for 3 h at 35 °C. Then, the polymerization was terminated by quenching with excess ethanol containing 5% HCl. The polymeric precipitate was filtered, and dried under vacuum to constant weight.

4.6. X-ray crystallographic study

Suitable single crystals of **2** were sealed in the thin-walled glass capillary for structural determination. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71070$ Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. The structure was solved by direct methods and refined by

full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structure was solved and refined using SHELEXL-97 program. Crystal data for **2**: $C_{66}H_{98}LiLuO_5Si_2$, $M_r = 1209.53$, crystal size $0.80 \times 0.60 \times 0.20$ mm, monoclinic, space group $P2_1/n$, $a = 11.202(1)$ Å, $b = 24.236(3)$ Å, $c = 24.973(3)$ Å, $\alpha = 90^\circ$, $\beta = 93.778(3)^\circ$, $\gamma = 90^\circ$, $V = 6765.2(14)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.188$ g cm⁻³, $\mu = 1.538$ mm⁻¹, $F(0\ 0\ 0) = 2544$, $T = 293(2)$ K, 59,410 collected, 12,337 independent reflections [$\max. 2\theta \leq 50.70$] and 617 parameters, $S = 1.164$, $R_1 = 0.0744$, $wR_2 = 0.1975$ [$I > 2\sigma(I)$], $R_1 = 0.1007$, $wR_2 = 0.2290$ (all data). There is an independent THF molecule in the unit cell.

Supplementary material

CCDC 709672 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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