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Tris(4-hydroxy-3,5-diisopropylbenzyl)amine as a new bridging ligand for novel trinuclear titanium complexes

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ABSTRACT

Tris(4-hydroxy-3,5-diisopropylbenzyl)amine (**LH_3**) was synthesized by the reaction of 2,6-diisopropylphenol and hexamethylenetetramine in the presence of *p*-toluenesulfonic acid or paraformaldehyde. Its solid state structure was determined by single crystal X-ray diffraction. Its fully deprotonated specie, (4-O-3,5-*i*-$Pr_2PhCH_2)_3N$ (**L**), was used to form novel trinuclear half-sandwich titanocene complexes, namely $[(\eta^5\text{-}C_5Me_5)TiCl_2]_3L$ (**1**) and $[(\eta^5\text{-}C_5Me_5)Ti(OMe)_2]_3L$ (**2**), which were then tested for the syndiospecific polymerization of styrene in the presence of methylaluminoxane (MAO) cocatalyst. Their catalytic properties were directly compared with those of trichloro(pentamethylcyclopentadienyl)titanium(IV) (**3**) and dichloro(2,6-diisopropylphenolato)(pentamethylcyclopentadienyl)titanium(IV) (**4**). **1**/MAO and **2**/MAO systems showed higher activities towards styrene polymerization than the mononuclear catalytic systems **3**/MAO and **4**/MAO, giving syndiotactic polystyrene of high molecular weight.

1. Introduction

The commercial importance of syndiotactic polystyrene (sPS) [1] (an engineering thermoplastic polymer with high melting point, good thermal and dimensional stability, low dielectric constant, and rapid crystalline rate [2]) has inspired to much effort to develop more effective catalysts for its polymerization [3,4]. A variety of half-sandwich titanium complexes have been tested as catalysts for the syndiospecific polymerization of styrene [5–14], including monocyclopentadienyltitanium complexes [5], monoindenyltitanium complexes [6], and their substituted derivatives [7–14]. Despite excellent initiators having been reported, the search for new catalysts for generating sPS remains of interest.

Multinuclear titanocene complexes with more than two linked active centers per molecule have shown cooperative catalytic properties in olefin polymerization [15]. They often show interesting catalytic behavior different from mononuclear systems. Multinuclear titanocene complexes as catalysts for polyolefins can be classified into four types depending on the nature of the bridging group (Fig. 1). Bridging groups can be multinuclear titanocenes, which comprise cyclopentadienyl rings connected by spacers (Fig. 1(a)) [16–28], multi-aryloxy or multi-alkoxy ligands linked by spacers (Fig. 1(b)) [29–31], Cp and aryl/alkyloxy mixed ancillary ligands connected by spacers (Fig. 1(c)) [32,33], or doubly bridged titanocene (Fig. 1(d)), which can employ two types of bridge (i.e. those in both Fig. 1(a) and (b)) [34]. Most previous work on multinuclear titanocene complexes has focused on dinuclear complexes [15–34], with much less attention directed towards the relationship between multinuclear complexes' structures and the types of polymerization they induce in comparison with well-known mononuclear systems. Although dinuclear titanocene catalysts connected by flexible or rigid bridging groups [15–34] and oxo-bridged trinuclear/tetranuclear titanocene [35,36] catalysts have been studied, to the best of the authors' knowledge, there are no reports of trinuclear titanocene catalysts with well defined aryloxy or alkoxy linkers.

To develop a trinuclear titanium complex for the catalysis of sPS formation, *N*-centered and C_3-symmetric tris(4-hydroxy-3,5-diisopropylbenzyl)amine (**LH_3**), derived from 2,6-diisopropylphenol and hexamethylenetetramine in the presence of *p*-toluenesulfonic acid or paraformaldehyde, was considered a suitable ligand because of its three diisopropylphenol moieties; various cyclopentadienyltitanium complexes with 2,6-diisopropylphenoxy ligands have been reported as good catalysts for polyolefins [37]. This paper reports the synthesis and characterization of novel trinuclear titanium complexes **1** and **2** linked by **L** and their syndiospecific polymerization of styrene. The solid state structure of ligand **LH_3** was also confirmed by single crystal X-ray diffraction.

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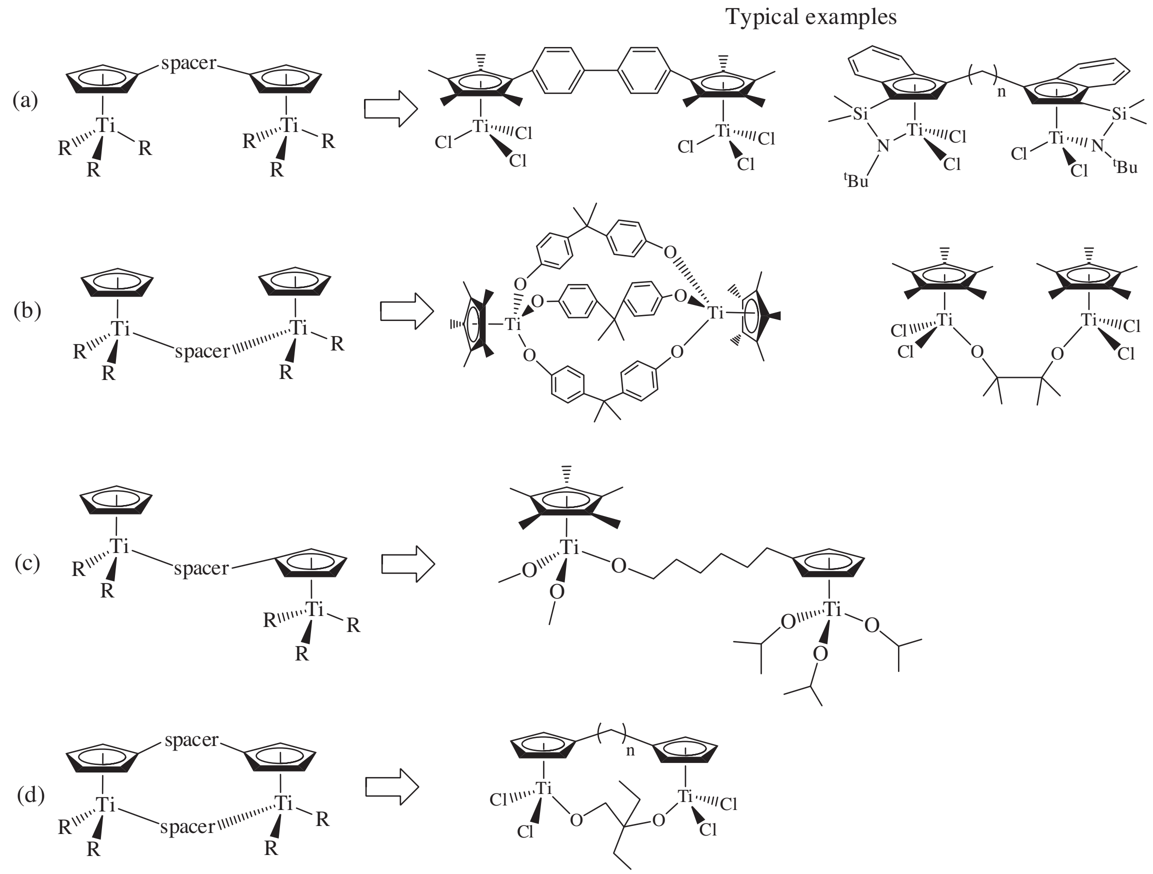


Fig. 1. Multinuclear titanocene complexes with different bridging groups: (a) cyclopentadienyl ring bridges, (b) multi-aryloxy or multi-alkoxy bridges, (c) Cp and aryl/alkyloxy mixed bridges, and (d) double bridges.

2. Experimental

2.1. General procedure

All reactions of air- and moisture-sensitive materials were carried out under dinitrogen atmosphere using standard Schlenk-type glassware on a dual manifold Schlenk line and glove box technique [38]. All solvents such as toluene, diethylether, and *n*-hexane were dried by distillation from sodium diphenylketyl under dinitrogen and were stored over 3 Å activated molecular sieves [39]. $CDCl_3$ was dried over 4 Å activated molecular sieves and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve [39]. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature on a Bruker DPX-300 NMR spectrometer using standard parameters. All chemical shifts are reported in δ units with reference to the residual peaks of chloroform-d_1 for proton (7.24 ppm) and carbon (77.0 ppm) chemical shifts. Elemental analyses were performed using an EA 1110-FiSONS analyzer (CE Instruments). The syndiotactic polystyrene polymers' thermal properties were investigated by Thermal Analyst 200 differential scanning calorimetry (DSC) system. *Ca.* 3–4 mg samples were heated to 300 °C under dinitrogen atmosphere at 10 °C/min, cooled at 10 °C/min to 30 °C, and finally reheated to 300 °C at 10 °C/min. The polymers' molecular weights and molecular weight distribution were determined at 140 °C in 1,2,4-trichlorobenzene by PL 220 + 220R GPC calibrated with standard polystyrenes.

2.2. Synthesis

All other chemicals were from Aldrich and were used as supplied unless otherwise indicated. 10% MAO in *n*-heptane was from Witco. $(\eta^5\text{-}C_5Me_5)TiCl_2(O\text{-}2,6\text{-}i\text{-}Pr_2Ph)$ (**4**) was synthesized by a reported procedure [40].

2.2.1. Synthesis of tris(4-hydroxy-3,5-diisopropylbenzyl)amine (**LH_3**)

(Route 1) A mixture of hexamethylenetetramine (1.40 g, 10.0 mmol), 2,6-diisopropylphenol (8.16 g, 45.8 mmol), and *p*-toluenesulfonic acid (0.1 g) was stirred and heated in an oil bath at 110 °C for 12 h. An additional quantity of 2,6-diisopropylphenyl (2.48 g, 13.9 mmol) was added and heated for a further 12 h. The resultant solid was recrystallized from acetone (20 mL) giving a colorless crystalline solid (5.20 g, yield = 88.5%).

(Route 2) A mixture of hexamethylenetetramine (1.40 g, 10.0 mmol), 2,6-diisopropylphenol (3.67 g, 30.0 mmol), and 37 wt% paraformaldehyde in water (2.45 mL, 30.0 mmol) in 50 mL methanol was stirred and refluxed for 2 days before being filtered. All volatiles were removed under vacuum and the residue was washed with 20 mL cold methanol. After recrystallization from diethylether at −20 °C in refrigerator, the desired product **LH_3** was obtained as colorless crystalline solid (3.33 g, yield = 56.7%).

^1H NMR ($CDCl_3$, 300.13 MHz, ppm): δ 7.10 (s, 6H, Ar*H*), 4.62 (br s, 3H, O*H*), 3.41 (s, 6H, NCH_2Ar), 3.17–3.07 (m, 6H, $CHMe_2$), 1.27 (d, J = 6.84 Hz, 36H, $CHMe_2$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz, ppm): δ 148.52, 133.18, 131.92, 123.58 (Ar), 57.59 (NCH_2Ar), 27.14 ($CHMe_2$), 22.92 ($CHMe_2$).

Anal. Calc. for $C_{39}H_{57}NO_3$: C, 79.68; H, 9.77; N, 2.38. Found: C, 79.85; H, 9.81; N, 2.29%.

2.2.2. Synthesis of $[(\eta^5\text{-}C_5Me_5)TiCl_2]_3L$ (**1**)

LH_3 (1.00 g, 1.70 mmol) in diethylether (30 mL) was treated with 3.3 equiv of *n*-butyllithium (5.61 mmol, 2.5 M solution in hexane) at −78 °C. The reaction mixture was then warmed to room temperature and stirred for 4 h. To the resulting solution, containing trilithium salt of the ligand **LH$_3$**, was added trichloro(pentamethylcyclopentadienyl)titanium(IV) (**3**) (1.62 g, 5.61 mmol) in diethylether (30 mL) via cannula at −78 °C. The reaction mixture was allowed to warm to room temperature over 2 h and stirred overnight. All volatiles were evaporated under vacuum, leaving a red-orange solid, to which 30 mL toluene was added. The solution was filtered, and the solvent evaporated to afford desired product **1** as a red-orange powder (1.79 g, yield = 78%).

^{1}H NMR (CDCl$_3$, 300.13 MHz, ppm): δ 7.40 (s, 6H, Ar*H*), 4.03 (s, 6H, NC*H*$_2$Ar), 3.24–3.15 (m, 6H, C*H*Me$_2$), 2.19 (s, 45H, C$_5$*Me*$_5$), 1.27 (d, *J* = 6.70 Hz, 36H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz, ppm): δ 160.04, 140.48, 133.11, 129.02, 126.50, 125.27, 123.34 (Ar and *C*$_5$Me$_5$), 54.77 (N*C*H$_2$Ar), 26.82 (*C*HMe$_2$), 24.08 (CH*Me*$_2$), 13.09 (C$_5$*Me*$_5$).

Elemental Analysis Calc. for $C_{69}H_{99}Cl_6NO_3Ti_3$: C, 61.53; H, 7.41; N, 1.04. Found: C, 61.68; H, 7.54; N, 1.12%.

2.2.3. Synthesis of [(η^5-C$_5$Me$_5$)Ti(OMe)$_2$]$_3$L (**2**)

LH$_3$ (0.71 g, 1.20 mmol) in 30 mL toluene was added dropwise to trimethanolato(pentamethylcyclopentadienyl)titanium(IV) (1.00 g, 3.62 mmol) in 20 mL toluene at room temperature. After overnight stirring, the resulting light yellow suspension was filtered and the filtrate was dried *in vacuo*, quantitatively affording **2** as a spectroscopically pure yellow powder. Recrystallization from concentrated *n*-hexane solution at −20 °C gave a yellow-orange powder **2** in 92% yield (1.74 g).

^{1}H NMR (CDCl$_3$, 300.13 MHz, ppm): δ 7.04 (s, 6H, Ar*H*), 4.08 (s, 18H, O*Me*), 3.37 (s, 6H, NC*H*$_2$Ar), 3.22–3.16 (m, 6H, C*H*Me$_2$), 2.01 (s, 45H, C$_5$*Me*$_5$), 1.20 (d, *J* = 6.63 Hz, 36H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz, ppm): δ 157.52, 136.35, 131.09, 123.01, 122.92 (Ar and *C*$_5$Me$_5$), 62.24 (O*Me*), 58.06 (N*C*H$_2$Ar), 25.83 (*C*HMe$_2$), 24.05 (CH*Me*$_2$), 10.86 (C$_5$*Me*$_5$).

Elemental Analysis Calc. for $C_{75}H_{117}NO_9Ti_3$: C, 68.23; H, 8.93; N, 1.06. Found: C, 67.95; H, 8.89; N, 1.09%.

2.3. X-ray structure determination of *LH$_3$*

Crystallographic assessment of **LH$_3$** was performed at ambient temperature using a Bruker APEXII CCD area detector diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Single crystal of suitable size and quality was selected and mounted on glass capillary using Paratone® oil and centered in the X-ray beam using a video camera. Multi-scan reflection data were collected using a frame width of 0.5° in *w* and θ with 5 s exposures per frame. Determination of cell parameters, data reduction, and empirical absorption corrections were conducted using the programs APEX2, SAINT and SADABS, respectively [41]. The structure of **LH$_3$** was solved by direct methods and refined to convergence using full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL program package [42]. The fact that diffraction data for **LH$_3$**, crystallized as a diethylether hemisolvate, were collected at room temperature makes crystal diffractions weak. Thus, the isopropyl groups with considerable thermal motion and certain atoms with extremely large U_{eq} values were observed. However, we believe these data are still valuable to investigate the molecular structure of **LH$_3$.** A view of the molecular structure of **LH$_3$** is shown in Fig. 2, drawn using the program DIAMOND [43]. Details of the crystallographic data and parameters are listed in Table 1.

2.4. Polymerization procedure

Polymerizations were carried out in 250 mL Schlenk flask under magnetic stirring. Toluene, the polymerization solvent, was distilled from sodium diphenylketyl under dinitrogen atmosphere immediately before use. Styrene monomers were distilled from calcium hydride under dinitrogen and maintained cold until used. Solid MAO was used; it was obtained by removing all volatiles from the MAO solution. Polymerizations were carried by sequentially injecting solid MAO, toluene, styrene, and the titanium compound into a 250 mL Schlenk flask under magnetic stirring at 50, 70, and 90 °C. Reactions were terminated by the addition of 50 mL methanol and 50 mL 10% HCl in methanol. The resulting precipitated polymer samples washed three times each with 200 mL methanol and dried *in vacuo* at 70 °C for 12 h. The polymer was extracted with refluxing 2-butanone for 12 h to determine syndiotactic index (*SI*) of the obtained sPS.

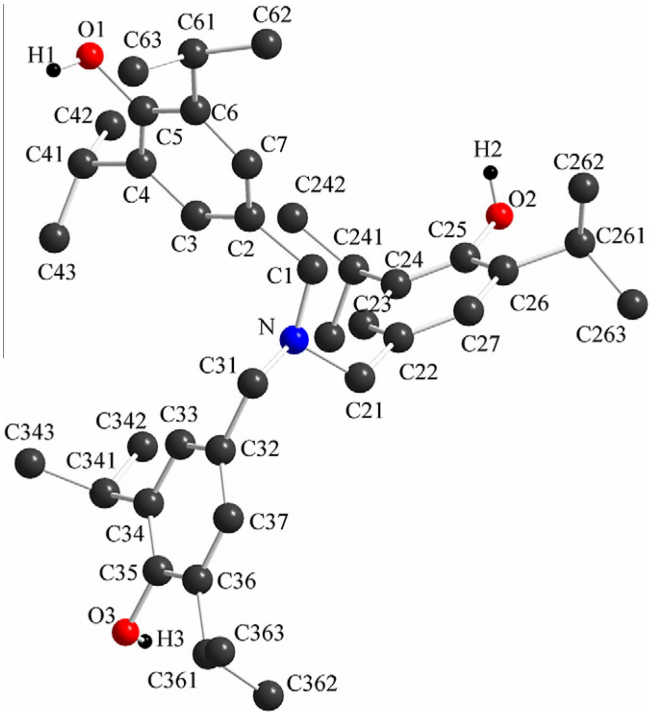


Fig. 2. Molecular structure of LH$_3$ with atom labeling (H atoms and Et$_2$O omitted for clarity).

3. Results and discussion

The ligand precursor **LH$_3$** was prepared by two different synthetic routes (Scheme 1) involving modified Mannich reaction between 2,6-diisopropylphenol and hexamethylenetetramine in the presence of *p*-toluenesulfonic acid (route 1) or paraformaldehyde (route 2) [44]. Route 1 gave **LH$_3$** with a much higher yield than route 2; however, it employed excess amount of 2,6-diisopropylphenol, which was then removed by recrystallization. The obtained **LH$_3$** was insoluble in hydrocarbons such as *n*-hexane and *n*-pentane but soluble in polar organic solvents. It was characterized by elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Recrystallization from diethylether gave **LH$_3$** as colorless crystals suitable for X-ray diffraction study. Its solid-state structure was determined by X-ray diffraction analysis (Fig. 2). Due to the atoms' slight thermal vibrations within the unit cells, caused by conducting crystallographic measurements at room temperature, the *R* indices for **LH$_3$** were somewhat high. **LH$_3$** crystallizes as a diethylether hemisolvate in the space group *C2/c*. **LH$_3$**, consisting of three 4-hydroxy-3,5-diisopropylbenzyl fragments connected by a nitrogen atom, has approximate three-fold symmetry. The large phenol bridging groups were oriented away from each other with suffi-

Table 1
Crystallographic data and parameter for **LH_3**.

	LH_3
Empirical formula	$C_{39}H_{57}NO_3 \cdot 0.5(C_4H_{10}O)$
Formula weight	624.92
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	
a (Å)	22.7335(19)
b (Å)	14.1790(11)
c (Å)	27.293(2)
α (°)	90
β (°)	110.802(2)
γ (°)	90
V (Å^3)	8224.1(11)
Z	8
ρ (g/cm^3)	1.009
μ (mm^{-1})	0.063
F(000)	2744
Index ranges	$-19 \leqslant h \leqslant 17$
	$-12 \leqslant k \leqslant 11$
	$-23 \leqslant l \leqslant 23$
θ (°)	$1.60 \leqslant \theta \leqslant 17.51$
Reflections collected	13 223
Independent reflections	2614
Number of observed reflections ($I > 2\sigma(I)$)	2074
Number of parameters refined	427
Goodness-of-fit (GOF) [$I > 2\sigma(I)$]	1.110
R_1 (all data)	0.0644
R_1 ($I > 2\sigma(I)$)[a]	0.0529
wR_2 (all data)	0.1847
wR_2 ($I > 2\sigma(I)$)[a]	0.1760

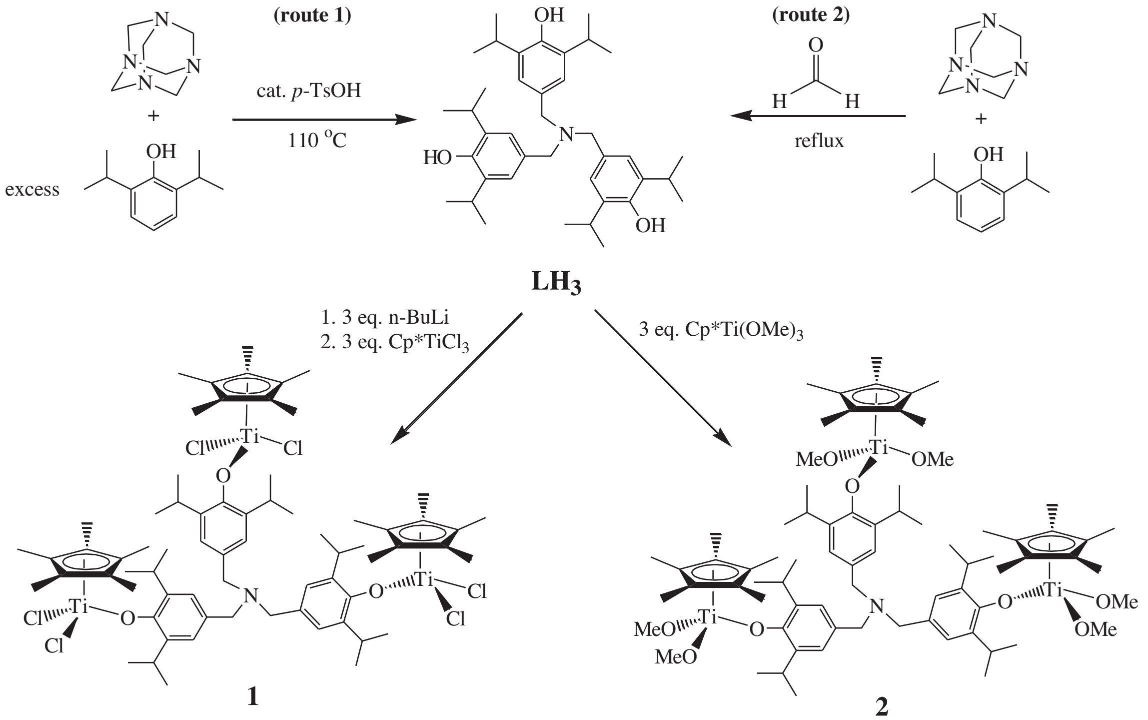
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

cient space for each phenol moiety to be coordinated to three titanium metal centers.

Transmetalation of the trilithium salt of **LH_3** with 3 equiv of trichloro(pentamethylcyclopentadienyl)titanium(IV) (**3**) in diethylether afforded the trinuclear titanium complex **1**, which contained one pentamethylcyclopentadienyl ligand, two chloro ligands, and a third part of **L** per titanium metal center. Trinuclear half-titanocene complex **2** with methanolato ligands was synthesized from the reaction of **LH_3** with 3 equiv trimethanolato(pentamethylcyclopentadienyl)titanium(IV). Compounds **1** and **2** were obtained as a red- or yellow-orange powders at yields of 78% and 92%, respectively. They were characterized by elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra are in accord with the suggested structures and all chemical shifts of the protons and carbon atoms appeared in the expected range. Measurement of **LH_3** alone in $CDCl_3$ established reference spectra for identifying the shifts of NMR peaks of **1** and **2**. Upon complexation to Ti, the proton resonances of **L** in complex **1** shifted downfield relative to those of **LH_3** due to the coordination of electron-withdrawing chloro ligands to the Ti. However, upfield shifted resonances were observed for complex **2** that contained electron-donating methanolato ligands. Despite their undetermined X-ray structures, **1** and **2** were still identified as trinuclear species bridged by fully deprotonated **L** due to the well defined spectroscopic data listed in Experimental section.

Because half-titanocenes are the most often used catalysts for sPS [3–14], the newly synthesized precursors **1** and **2** were examined as catalysts for syndiospecific polymerization of styrene in the presence of MAO cocatalyst, which was used in the solid state for reproducibility of activity. Polymerization results are listed in terms of catalytic activity, *SI*, melting temperature (T_m), M_w, and M_w/M_n (Table 2). The polymerization reaction was characterized by carrying out polymerizations at 50, 70, and 90 °C at a fixed MAO contents with [Al]/[Ti] = 1000. To compare catalytic properties with those of mononuclear catalysts, polymerizations with **3** and **4** (Fig. 3) were also performed under similar conditions (Table 2).

The polymerization results (Table 2) show that the trinuclear half-sandwich titanocenes **1** and **2** behave as highly active, single-site catalysts for styrene polymerization. The resulting polystyrene's *SI* and T_m are indicative of well maintained syndiospecific stereocontrol. Polystyrene produced by trinuclear complexes also showed a narrow M_w/M_n of about 2, similar to that obtained using



Scheme 1. Synthetic routes to **LH_3**, **1**, and **2**.

Table 2
Data for the syndiospecific polymerization of styrene using **1**–**4**.[a]

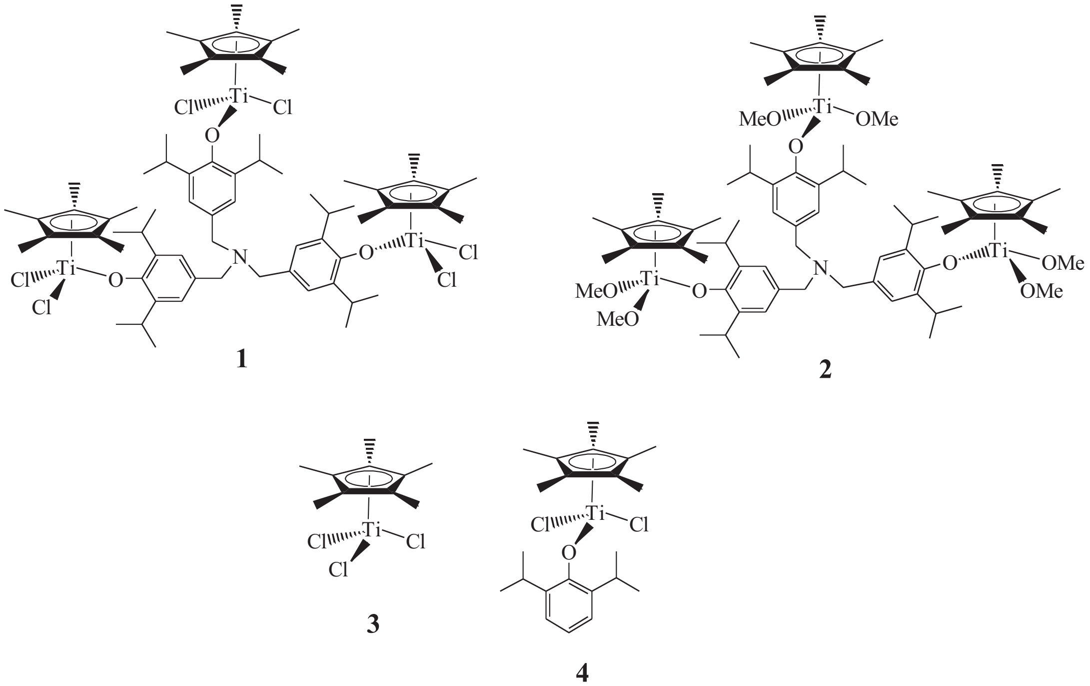
Cat.	T_p (°C)	Yield (g)	A ($\times 10^{-3}$) [b]	SI (%) [c]	T_m (°C)[d]	M_w ($\times 10^{-3}$) [e]	M_w/M_n[e]
1	50	1.91	13.5	98	271	523	1.8
	70	2.26	15.9	97	269	324	2.0
	90	2.05	14.5	95	270	140	1.9
2	50	4.22	29.8	98	272	662	2.5
	70	4.52	31.9	100	270	259	2.7
	90	4.37	30.8	98	271	113	2.6
3	50	0.84	5.93	100	268	485	1.6
	70	2.01	14.2	95	271	356	1.6
	90	1.99	14.0	93	271	168	1.7
4	50	1.09	7.69	100	271	439	1.9
	70	1.94	13.7	98	270	225	1.7
	90	1.97	13.9	98	268	113	2.0

[a] Polymerization Condition: styrene = 5.0 mL (43.6 mmol); Ti = 0.0195 mmol; Al/Ti = 1000; time = 10 min; toluene = 50 mL.
[b] Activity = kg of sPS/(mol of Ti · mol styrene · h).
[c] SI = syndiotactic index was determined from the amount of polymer insoluble in 2-butanone.
[d] Determined by DSC.
[e] Determined by GPC.

the mononuclear complexes **3** and **4**, which suggests that the three titanium centers in trinuclear complexes were identical and behaved as independent single active sites. Trinuclear **2**/MAO showed the highest catalytic activity among the four tested systems. The trinuclear complexes **1** and **2** showed higher catalytic activity than mononuclear systems **3** and **4** during polymerization at 50 and 70 °C. These results suggest that electronic stabilization arising through the rigidity of the bridging ligand **L** increased catalytic activity, indicating that **L** groups act as effective bridges for catalysis.

The polymerization temperature considerably affected the catalysts' efficiencies (Fig. 4(a) and Table 2), with catalytic activity being ranked **3**/MAO < **4**/MAO < **1**/MAO < **2**/MAO at 50 °C, **3**/MAO ~ **4**/MAO < **1**/MAO < **2**/MAO at 70 °C, and **3**/MAO ~ **4**/MAO ~ **1**/MAO < **2**/MAO at 90 °C. Interestingly, **1**/MAO, **3**/MAO, and **4**/MAO showed similar activity at 90 °C and the activity of **2** was consistently greater than that of **1**, while the mononuclear analogues **3** and **4** exhibit similar activity. Each system, except **4**/MAO, showed optimal catalytic activity at 70 °C. The activities of **1**/MAO and **2**/MAO increased similarly as the temperature rose from 50 to 70 °C; they also showed similar decreases with further heating to 90 °C. The activity of 3/MAO rapidly increased with heating to 70 °C and slowly decreased as the temperature was raised from **1**/MAO and **2**/MAO systems, rapid increase from 50 to 70 °C and slowly decrease from 70 to 90 °C. The catalytic activity of **4**/MAO increased with temperature at all the tested temperature.

Complexes **1**–**4** yielded sPS with M_w of 140 000–523 000, 113 000–662 000, 168 000–485 000, and 113 000–439 000, respectively. The polymerization temperature had a significant effect on the molecular weights of sPS (Fig. 4(b)), with M_w being ranked **4**/MAO < **3**/MAO < **1**/MAO < **2**/MAO at 50 °C, **4**/MAO < **2**/MAO < **1**/MAO < **3**/MAO at 70 °C, and **2**/MAO ~ **4**/MAO < **1**/MAO < **3**/MAO at 90 °C. **1**/MAO and **2**/MAO are notable in their production of sPS with ultrahigh molecular weight of 662 000 and 523 000, respectively, at 50 °C. The resulting sPS' molecular weight decreased in all cases with increasing polymerization temperature. At 50 °C, **2**/MAO generated the highest molecular weight sPS, while at 70



1 **2** **3** **4**

Fig. 3. Complexes **1**–**4**.

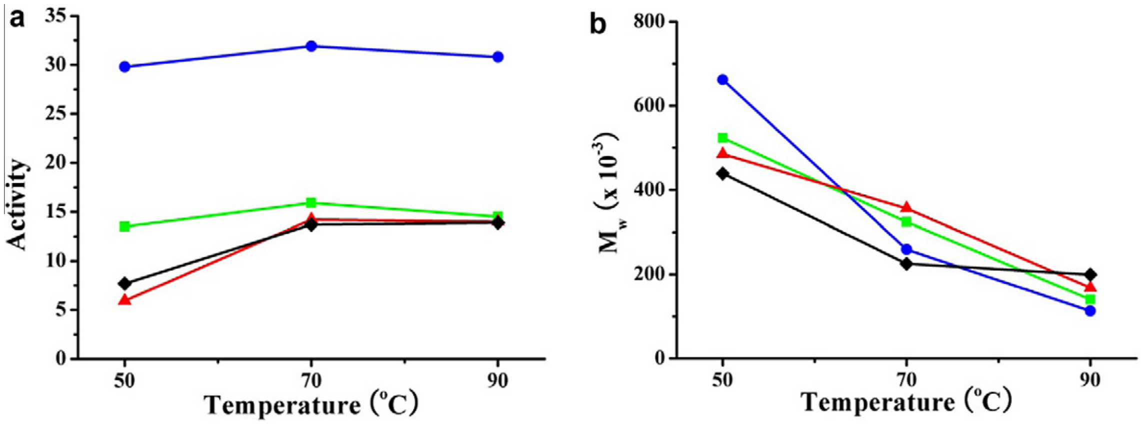


Fig. 4. (a) Catalytic activities and (b) M_w of sPS vs. polymerization temperature. ■, **1**/MAO; ●, **2**/MAO; ▲, **3**/MAO; ♦, **4**/MAO.

and 90 °C, mononuclear **3**/MAO generated the highest molecular weight polymers. This can be explained in terms of the ligands' steric effects: β-H elimination became preferable to propagation with increasing steric hindrance between the polymer chains and the ligands in the half-sandwich metallocenes [4]. Similar to the catalysts' activities, higher polymer molecular weights resulted from **2**/MAO rather than **1**/MAO at 50 °C.

To determine the polymers' *SI*, they were extracted with refluxing 2-butanone for 12 h. All systems afforded sPS with high *SI* values of 93–100% and T_m values of 268–272 °C under all tested conditions. None of the four MAO systems showed significant lowing of T_m with increasing polymerization temperature, as is often observed with homogeneous metallocene catalysts [3,4]. *SI* values were not correlated with polymerization temperature.

In Summary, trinuclear half-sandwich titanocene complexes bridged by fully deprotonated tris(4-hydroxy-3,5-diisopropylbenzyl)amine were prepared. In the presence of MAO cocatalyst, they showed enhanced activity towards the syndiospecific polymerization of styrene compared with monomeric half-sandwich complexes. Polymerization at 50 °C resulted in high molecular weight polymers; the polymers' molecular weights decreased significantly at higher polymerization temperatures. These results appear to be due to the combination of the electronic effects of the three cationic metal centers through the deprotonated tris(4-hydroxy-3,5-diisopropylbenzyl)amine bridges and/or the steric effects between them.

Acknowledgments

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Appendix A. Supplementary data

CCDC 844841 contains the supplementary crystallographic data for **LH₃**. 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.

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