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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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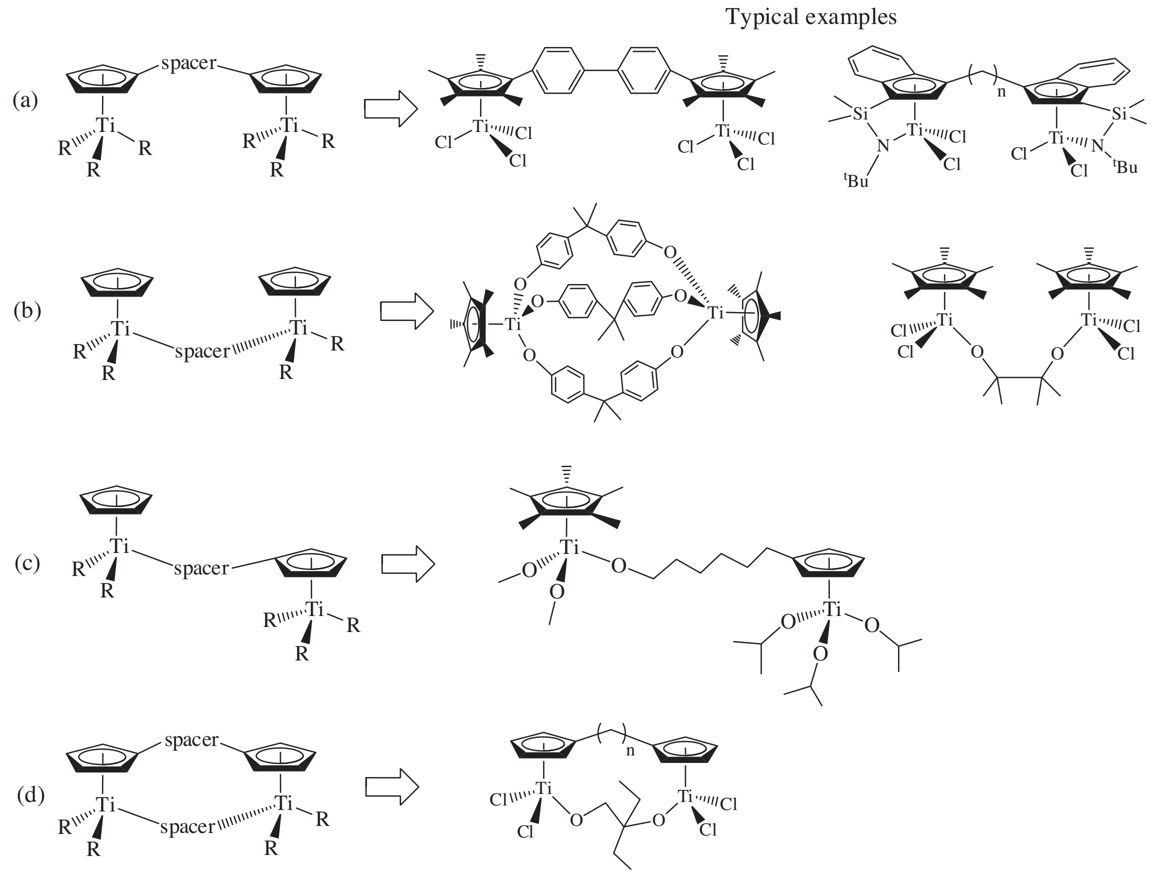

Fig. 1. Multinuclear titanocene complexes with different bridging groups: (a) cyclopentadienyl ring bridges, (b) multi-aryloxy or multi-alkoxy bridges, (c) Cp and aryl/alkyloxy mixed bridges, and (d) double bridges.

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