



Highly selective trimerization of ethylene with half-sandwich cyclopentadienyl and indenyl titanium complexes bearing pendant thienyl group



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ABSTRACT

A series of half-sandwich titanium complexes bearing thienyl group [Cp(Ind)-bridge-thienyl]TiCl₃ (**CS1–CS10**) have been synthesized and show high selective ethylene trimerization to 1-hexene. The molecular structure of **CS8** [Ind-C(*cyclo*-C₅H₁₀)-(5-Me-thienyl)]TiCl₃ was confirmed by X-ray. No intramolecular coordination interaction between the sulfur atom on the thienyl group and the titanium center could be observed in the solid state of these complexes. After activated with MAO, the complexes can effectively catalyze ethylene trimerization. For [Cp-bridge-thienyl]TiCl₃/MAO system, the best productivity is obtained at 30 °C; increasing the bulk of the substituent on the 5-position of the thienyl can improve the productivity for 1-hexene. **CS6** [Cp-C(*cyclo*-C₅H₁₀)-(5-SiMe₃-thienyl)]TiCl₃ upon with MAO can make a productivity of 553 kg/(mol Ti-h) and 1-hexene selectivity of 86% at 30 °C, 0.5 MPa ethylene pressure. For [Ind-bridge-thienyl] TiCl₃/MAO system, catalysts have more active and more tolerant of temperature comparing to corresponding Cp complexes. For example, **CS8** can make the productivity of 697 kg/(mol Ti-h) and 1-hexene selectivity of 95% at 80 °C, 0.5 MPa ethylene.

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1. Introduction

Linear alpha olefins (LAOs) as ethylene oligomerization products have a variety of applications including as co-monomers for the copolymerization with ethylene to generate linear low-density polyethylenes (LLDPEs) and as versatile intermediates for many industrially consumer products like plasticizers, lubricant, detergents, and surfactants. Conventional full-range production technology of ethylene oligomerization normally results in a wide mixture distribution and don't match the continually increasing market demand. Thus, the transformation of a statistical ethylene oligomerization process into selective tri- or tetramerization appears highly desirable [1,2].

Up to now, several chemical elements including chromium, titanium and tantalum as interesting catalysts have been reported for selective trimerization or tetramerization of ethylene to α -olefins [3–12]. Among all the catalysts systems, the central metal based on chromium, is widely studied in recent years, such as Phillips' Cr-pyrrolide catalysts [5], BP's *o*-OMePNP catalysts [13], Sasol's PNP/SNS trimerization catalysts [14,15] and PNP tetramerization

catalysts [16] and a series of self-activating catalysts from Gambatotta group [17–20].

Contrary to various of Cr-catalysts, catalyst systems that are based on titanium are relatively less. The arene-substituted cyclopentadienyl (Cp) titanium catalysts firstly reported by Hessen and co-workers in 2001 were the most attractive ethylene trimerization catalysts (Chart 1, 1) [9,10]. Systematic research work has been carried out on kinetic studies to optimize the reactions and theoretical studies to give the mechanistic description about this system [21,22]. The intrinsic high selectivity for ethylene trimerization essentially depends on the hemilabile behavior of the Cp-arene ancillary ligand. Other group IV metals: Zr and Hf compounds (Chart 1, 2) with similar ligands were also tested, but the result exhibit that the major product is polyethylene (PE) [23]. Recently Kim has reported a kind of tetradentate trianionic triethoxyamine titanate compound with the Cp-arene ligand (Chart 1, 3), which can obtain 92.3 wt.% ethylene trimerization selectivity and 1.03×10^4 kg/(mol Ti-h) 1-hexene productivity [24]. Suzuki also reported a series of new titanium complexes derived from FI catalyst bearing phenoxy-imine ligand with pendant aryl-OMe donors (Chart 1, 4). In the present of MAO, these complexes can selectively transform ethylene to 1-hexene with unprecedented high productivity (3.15×10^5 kg/((mol Ti-h)); and more insight studies are just in progress [25].

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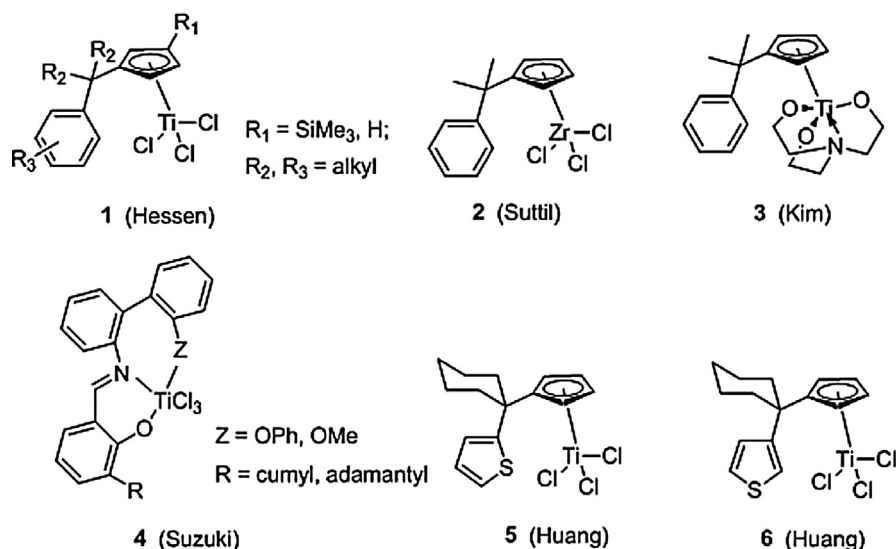


Chart 1. Typical ethylene trimerization catalysts based on group IV metals.

Following Hessen's Cp-bridge-arene ligand system, Huang's group successfully developed a half-sandwich titanium complex bearing pendent thienyl group (Chart 1, 5), which can serve efficiently for ethylene trimerization [26]. But the complex with bridge linked to the 3-position of the thienyl group (Chart 1, 6), is not effective for ethylene trimerization. The findings indicate that whether the coordination of metal center with sulfur atom is an important factor in the selective ethylene trimerization.

However, up to now no more detail information is discussed about the Cp-bridge-thienyl system. So it is necessary to study the influence of different hemilabile coordination situations on ethylene trimerization. For the system of [Cp-bridge-thienyl]TiCl₃/MAO, the elements that influence the coordination include the bridge, which can determine the orientation of thienyl group relative to the metal center, and the substituents on the thienyl group especially at 5-position, which can give a direct steric and electronic effect on the coordination between the sulfur and central metal. Besides them, regarding the diversity and flexibility of indenyl ring, it is helpful to understand the different steric and electronic effects on catalytic trimerization behavior when replacing Cp ring with indenyl ring.

Herein, to give a comprehensive understanding about the [Cp-bridge-thienyl] TiCl₃/MAO system, a series of new half-sandwich Cp titanium complexes with different bridges and different substituents on the thienyl group and also corresponding indenyl titanium complexes are synthesized and used for ethylene trimerization to further discuss the influence of different hemilabile coordination conditions between sulfur atom and central metal on ethylene trimerization.

2. Experimental

2.1. General considerations

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified by distillation over sodium benzophenone (diethyl ether, tetrahydrofuran, toluene and n-hexane) and P₂O₅ (dichloromethane). MAO (toluene solution, 1.53 M) was produced by Crompton. Polymerization grade ethylene was used without further purification. 6,6-dialkylfulvenes [27], Benzofulvenes [28], substituted thiophenyl lithium [29–31], 2-trimethylsilyl thiophene [31], and 5 [26] were synthesized according to the literature.

NMR was measured on a Bruker AVANCE-400 Hz spectrometer using tetramethylsilane (TMS) as an internal standard and employing CDCl₃ as solvent dried over the standard drying agent for a minimum of 24 h. Elemental analyses were performed on an EA-1106 spectrometer. GC-MS was performed on 6890N-5975 instrument. GC was performed on Fuli 9790 instrument equipped with Agilent J&W HP-5 GC column. IR spectra were recorded on a Nicolet FTIR 55XC spectrometer. Melting point were tested on XGW x-4 micro melting point instrument.

2.2. Synthesis of complexes CS1–CS10

2.2.1. Synthesis of CS1: [$\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_4\text{H}_3\text{S}$]TiCl₃

To a solution of 21 mmol of 2-thienyl lithium in 40 mL of diethyl ether was added dropwise 2.2 g (21 mmol) of 6,6-dimethylfulvene. The reaction mixture was stirred overnight. 2.25 g (21 mmol) of trimethylsilyl chloride in 10 mL THF was added. The mixture was stirred overnight, and then poured into 100 mL of ice-water. The water layer was extracted with 30 mL of Et₂O, after which the combined organic layers were rinsed with 100 mL of brine. The organic phase was dried over MgSO₄. After the solvents were evaporated in vacuum, the residue was distilled to give C₅H₄(SiMe₃)CMe₂C₄H₃S (**LS1**) in yield of 42% (2.3 g, 80–95 °C/0.2 mmHg). ¹H NMR (400 MHz, CDCl₃) δ : 7.12 (m, 1H, thienyl-H), 6.88 (m, 1H, thienyl-H), 6.73–6.82 (m, 1H, thienyl-H), 6.40 (m, 2H, Cp-H), 6.11 (m, 1H, Cp-H), 3.25 (s, 1H, Cp-H), 1.64 (s, 6H, CH₃), –0.03 (m, 9H, Si-CH₃).

To a solution of 0.50 mL of TiCl₄ (4.6 mmol) in 20 mL of CH₂Cl₂, cooled to 0 °C, was added dropwise a solution of 1.20 g (4.6 mmol) of C₅H₄(SiMe₃)CMe₂C₄H₃S (**LS1**) in 10 mL of CH₂Cl₂. The mixture was warmed to room temperature and stirred over night. The methylene chloride was removed in vacuum, and the residue was extracted with petroleum ether. Cooling the filtrate to –30 °C yielded red crystals of **CS1** (420 mg, 27%). mp: 57.3–59.1 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.17 (m, 1H, thienyl-H), 6.91 (m, 1H, thienyl-H), 6.83 (m, 1H, thienyl-H), 7.07 (t, *J* = 2.8 Hz, 2H, Cp-H), 6.87 (t, *J* = 2.8 Hz, 2H, Cp-H), 1.92 (s, 6H, CH₃). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ : 153.06, 152.96, 126.81, 124.25, 123.54, 123.38, 121.37, 39.66, 30.13. IR (KBr, cm⁻¹): 3102, 2970, 2925, 1474, 1415, 1381, 1360, 1259, 1228, 1143, 1046, 847, 828, 758. Anal. Calc. for C₁₂H₁₃Cl₃Si: C, 41.96; H, 3.81; Found C, 42.50; H, 3.74.

2.2.2. Synthesis of complex CS2: [$\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_4\text{H}_2\text{S}(\text{Me})$]TiCl₃

The same procedure as described for **LS1** was used. 28 mmol of 2-methylthienyl lithium, 3.00 g (28 mmol) of 6,6'-dimethylfulvene

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