

Synthesis and characterization of titanium alkyl, oxo, and diene complexes bearing a SiMe₂-bridged phenoxy-cyclopentadienyl ligand and their catalytic performance for copolymerization of ethylene and 1-hexene

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Dedicated to Professor G. Erker on the occasion of his 60th birthday.

Abstract

A series of titanium complexes bearing a SiMe₂-bridged phenoxy-cyclopentadienyl ligand were synthesized and characterized, and their catalytic behavior for copolymerization of ethylene and 1-hexene was investigated. Treatment of dimethylsilyl(2,3,4,5-tetramethylcyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy)-titanium dichloride (**1**) with appropriate nucleophiles afforded dimethoxy complex **2**, dimethyl complex **3**, and dibenzyl complex **4**. Standing a toluene solution of **2** in air afforded a dinuclear μ -oxo complex **5** as a single isomer. 1,3-Diene complexes **6–8** were prepared by reaction of **1** with the corresponding 1,3-dienes in the presence of 2 equiv. of *n*-BuLi. X-ray analysis of 1,4-diphenyl-1,3-butadiene complex **6** revealed that the diene ligand coordinates to titanium in *s-cis* fashion with a prone orientation. The newly prepared titanium complexes were applied to copolymerization of ethylene and 1-hexene upon activation with Al^{*i*}Bu₃ and [C₆H₅NMe₂H][B(C₆F₅)₄]. It was found that the alkyl complexes **3–4** and the diene complexes **6–8** showed higher activities than **1** at elevated temperature.

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Keywords: Titanium complex; Cyclopentadiene; Phenolate; Diene; Polymerization

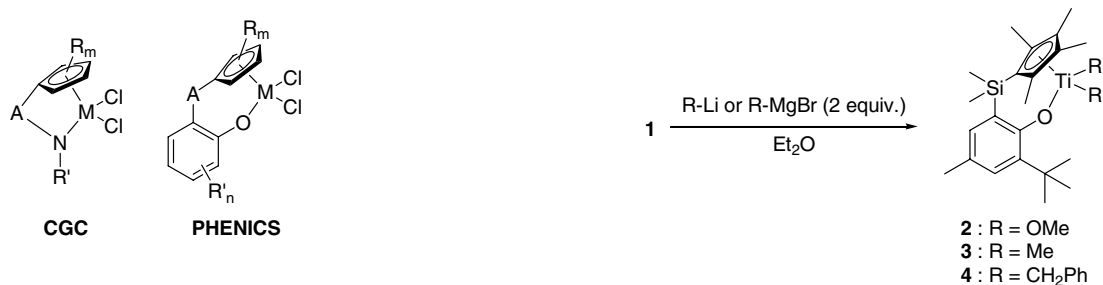
1. Introduction

Alkene polymerization catalyst systems based on metallocene and half-metallocene complexes of early transition metals have attracted special interest in the past two dec-

ades because their homogeneous aspect enabled tunable ligand design of catalysts for precise control of polymer microstructure, copolymerization, and so on [1]. Among the developed catalysts, bridged cyclopentadienyl amide complexes (CGC: constrained geometry catalyst) [2] and bridged phenoxy complexes (PHENICS: phenoxy-induced complex of Sumitomo) [3] are two of the industrially important catalyst systems that produced new unpredicted elastomers starting from α -olefins.

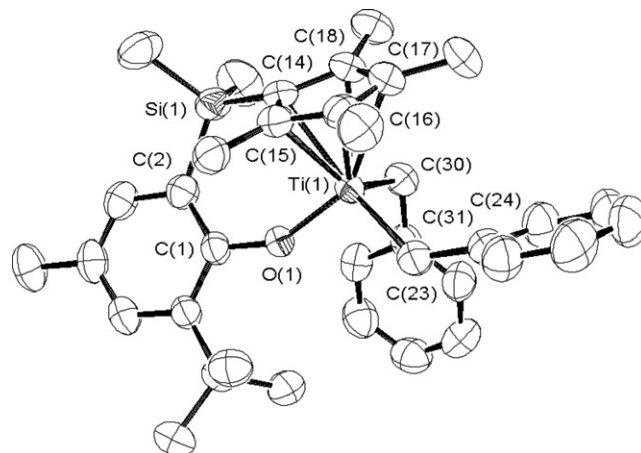
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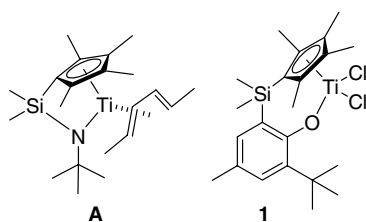
Scheme 1.

Alkyl groups have been reported as novel leaving substituents, leading to smooth generation of active species. Dimethyl and dibenzyl titanium complexes with Me₂Si(η⁵-C₅Me₄)(^tBuN) ligand showed higher activities than dichloro complex upon activation with borate cocatalyst [4]. 1,3-Butadiene derivatives are known to coordinate to early transition metals in various orientations [5], and diene ligand was readily activated to give catalytically active species [6–9]. Erker reported that 1,3-butadiene metallocene complexes readily reacted with B(C₆F₅)₃ to afford zwitterionic complexes which were applied to polymerization of α-olefin as well as detailed mechanistic study of olefin polymerization [7]. Marks and his coworkers synthesized a series of 1,3-butadiene CGC complexes in which the orientation of the diene moieties (prone/supine) was reported to depend on not only ligand architectures but also bulkiness of diene ligand [8]. They also reported that prone complex (A) showed high activity for copolymerization of ethylene and 1-octene upon activation with B(C₆F₅)₃. We report herein synthesis of alkyl, diene and methoxy derivatives of a SiMe₂-bridged PHENICS **1** and X-ray analyses of representative complexes. We also demonstrate copolymerization behavior of ethylene and 1-hexene using these newly prepared complexes.

Fig. 1. ORTEP drawing of the molecular structure of **4**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

selected bond parameters are summarized in Table 1. The dibenzyl complex **4** adopts three-legged piano stool geometry. Two angles of Ti–C–C(*ipso*) (112.13° and 130.0°) are much different: one of two benzyl groups coordinates in an η¹-fashion to the titanium atom, while the other in an η²-fashion in order to compensate the coordinative unsaturation around the titanium atom Schemes 2–4.

The dimethoxy complex **2** is moisture sensitive, and standing a toluene solution of **2** in air afforded a dinuclear μ-oxo complex **5** (76% yield), formed by hydrolysis of one



2. Results and discussion

Scheme 1 shows the synthesis of alkyl and methoxy titanium complexes **2–4**. A suspension of **1** in ether was treated with a solution of 2 equiv. of a nucleophile such as MeOLi, MeLi, or PhCH₂MgBr in ether at –78 °C. After removal of inorganic materials at room temperature, crystallization from hexane gave the corresponding complexes **2** (70% yield), **3** (68% yield), and **4** (63% yield). Complexes **2–4** were characterized by NMR and elemental analysis. Structure of the dibenzyl complex **4** was further determined by X-ray analysis. Fig. 1 shows an ORTEP diagram, and

Table 1
Selected bond length (Å) and angles (°) for **4**

Bond lengths (Å)			
Ti(1)–C(30)	2.154(3)	Ti(1)–C(23)	2.135(3)
Ti(1)–O(1)	1.812(2)	Ti(1)–C(14)	2.287(2)
Ti(1)–C(15)	2.327(2)	Ti(1)–C(16)	2.421(3)
Ti(1)–C(17)	2.442(2)	Ti(1)–C(18)	2.384(2)
Bond angles (°)			
C(23)–Ti(1)–C(30)	102.5(1)	O(1)–Ti(1)–C(23)	102.5(1)
O(1)–Ti(1)–C(30)	102.2(1)	C(24)–C(23)–Ti(1)	130.0(2)
C(31)–C(30)–Ti(1)	112.1(2)	O(1)–Ti(1)–C(14)	90.80(9)
O(1)–Ti(1)–C(15)	89.83(9)	O(1)–Ti(1)–C(16)	120.1(1)
O(1)–Ti(1)–C(17)	146.33(8)	O(1)–Ti(1)–C(18)	123.9(1)
C(1)–O(1)–Ti(1)	150.3(2)	C(14)–Si(1)–C(2)	110.1(1)
Torsion angles (°)			
C(14)–Si(1)–C(2)–C(1)	–19.2(2)	Ti(1)–O(1)–C(1)–C(2)	11.8(5)

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