Catalytic trimerization of ethylene by half-sandwich titanium complexes bearing a pendant ethereal group

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Abstract

Three half-sandwich titanium complexes with a pendant ethereal group, $CH_3OCH_2CH_2CpTiCl_3$, $CH_3OCH(CH_3)CH_2CpTiCl_3$, and tetrahydrofurfurylcyclopentadienyltitanium trichloride activated by MAO have been found to trimerize ethylene with high selectivity and moderate activity. Compared with the catalytic behavior of $CpTiCl_3$/MAO and n-Pr-$CpTiCl_3$/MAO, we can identify that the pendant ethereal group plays an important role in this selective trimerization process. Their different catalytic behavior toward temperature is discussed.
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1. Introduction

Cyclopentadienyl ligands have been studied intensively as the most important ligands in organometallic chemistry. Special attention on this area is focused on modifying the Cp ring by introducing a pendant group that can coordinate to the metal center [1]. If the pendant group only interacts weakly with the metal center as a labile group, this system is a so-called hemilabile ligand. Hemilabile ligands are expected to affect dramatically the properties of organometallic catalyst [2].

Half-sandwich titanium complexes are well-known as catalyst precursors in combination of MAO(methylalumoxane) for olefin polymerization, especially for styrene [3]. Recently, Hessen and coworkers reported that half-sandwich titanium complexes with a pendant arene group can act as a precursor for selective trimerization of ethylene to 1-hexene with high activity [4]. Hessen and co-workers proposed that the arene-cyclopentadienyl ligand was likely to exhibit hemilabile behavior that might be responsible for selective trimerization of ethylene.

Half-sandwich titanium complexes **1**–**3** with a pendant ethereal group were first synthesized in our laboratory [5] (Scheme 1).

Intramolecular coordination of the oxygen atom to the metal center in complexes **1**, **2** has been revealed by IR and X-ray diffraction. But in complex **3**, the oxygen atom is not coordinated to the titanium center, which was indicated by IR data. Although the oxygen atom in complex **1** is coordinated to the titanium center in its solid state, this intramolecular coordination of the ethereal moiety was found to be fluxional in solution by van der Zeijden [6]. At room temperature, only 30% of compex **1** is in a conformation in which the ether group is coordinated. This indicates that the interaction between the oxygen donor and the titanium center is relatively weak, although the oxygen atom is a harder Lewis base than the arene group mentioned above. Herein, it is envisaged that the pendant o-donors may behave as a labile group and that titanium complexes **1**–**3** with an ethereal–pendant cyclopentadienyl ligand can act as catalyst precursors for trimerization of ethylene. With this idea, the complexes **1**–**3** with MAO cocatalyst were examined in ethylene conversion in comparison with the reference catalysts $CpTiCl_3$/MAO and n-$PrCpTiCl_3$/MAO.
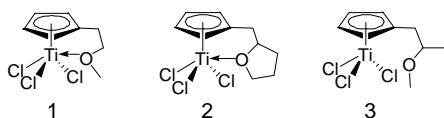
2. Experiment

2.1. Materials

Complexes **1**–**3** were prepared according to reference [5]; toluene was distilled from sodium prior to use. Polymeriza-

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Scheme 1.

tion grade ethylene was used without further purification; A solution of MAO in toluene was purchased from Akzo Nobel.

2.2. Apparatus

GC was performed on a Shimadzu-14B instrument equipped with a SE-30 column (30 m × 0.25 mm) and a flame ionization detector. GC–MS analyses were conducted using a HP5973 mass-selective detector attached to a HP 6890 GC instrument.

2.3. Procedure for ethylene conversion

A 100 ml autoclave, equipped with a magnetic stirring bar, was preheated at 100 °C under vacuum for 30 min and then cooled to the required temperature. Toluene (20 ml) was injected into the reactor and pressured with ethylene to 5 atm. After equilibrating for 20 min, the appropriate volume of catalyst solution and MAO were injected to start the reaction. The ethylene pressure was kept constant during the reaction. After the designated run time, the reactor was vented and the reaction mixture was quenched by ethanol. n-Heptane was added to the mixture as an internal standard for GC analysis. An upper-layer clear solution was seperated from the reaction mixture to analyze and quantify the soluble components by GC and GC–MS. The polymer was stirred in acidic ethanol for 10 min, then rinsed with ethanol for several times and dried under vacuum.

3. Results and discussion

The results are shown in Table 1. As we expected, **1**–**3**/MAO are all able to trimerize ethylene with high se-

lectivity (entry 2, 4, 5, 6). In these cases, the selectivity of 1-hexene was high (>90%). No other oligomers, such as butene and octene were detected, and a little polymer was produced. **2**/MAO shows the highest activity (57 kg $(mol Ti)^{-1} h^{-1}$) and selectivity(>95%) at 80 °C.

From the results shown in Table 1, we also noticed that the catalytic behavior of **1**–**2**/MAO is strongly temperature-dependant. At 30 °C, both **1**/MAO and **2**/MAO are inactive for ethylene oligomerization. Remarkably, when the temperature was raised to 80 °C, they exhibited considerable activity. In the case of **3**/MAO, the situation is different. At 30 °C, 1-hexene was also produced as the predominant product with activity of 25 kg $(mol Ti)^{-1} h^{-1}$. Noticeable variation in the catalytic behavior of **3**/MAO was not found when the reaction temperature was raised from 30 to 80 °C.

In contrast, in the case of CpTiCl$_3$/MAO (entries 7 and 8), the predominant product was polymer, although 1-hexene was also produced at 30 °C. It can be seen that n-PrCpTiCl$_3$/MAO (entries 9 and 10) exhibited the catalytic behavior similar to that of CpTiCl$_3$/MAO. This suggests that an alkyl side chain attached to the Cp ring does not considerably affect the behavior of the catalyst.

Thus, a conclusion can be drawn that the pendant ethereal group in complexes **1**–**3** plays an important role in selective trimerization of ethylene. The ethereal–pendant cyclopentadienyl ligand is likely to exhibit hemilabile behavior in ethylene trimerization, stabilizing the electron-deficient titanium center by the intramolecular coordination of oxygen atom and slipping to make room for the incoming ethylene.

Complexes **1** and **2** upon activation with MAO form cationic complexes in which the oxygen atom is likely to coordinate to the metal center. As mentioned above, in complexes **1** and **2**, the coordination of oxygen atom is fluxional in solution, but this coordination becomes stronger after **1** and **2** are activated by MAO because the generated cationic titanium center becomes more electron-deficient. At low temperature, the oxygen atom of the ethereal group occupies the coordination site of the titanium center stably, which inhibits ethylene coordination, so **1**–**2**/MAO are inactive. When the temperature is raised, the coordination of oxygen atom become fluxional or labile, and the

Table 1
Results of ethylene conversion with **1**–**3**/MAO, CpTiCl$_3$/MAO and n-PrCpTiCl$_3$/MAO

Entry	Catalyst	Temperature (°C)	1-Hexene (g)	PE (g)	Productivity 1-hexene[a]	Selectivity of 1-hexene (wt.%)
1	**1**	30	Trace	0.050	/	/
2	**1**	80	0.038	0.004	25	90
3	**2**	30	Trace	Trace	/	/
4	**2**	80	0.080	Trace	57	>95
5	**3**	30	0.042	0.004	25	93
6	**3**	80	0.046	0.004	28	92
7	CpTiCl$_3$	30	0.015	0.220	10	6
8	CpTiCl$_3$	80	Trace	0.284	/	/
9	n-PrCpTiCl$_3$	30	0.012	0.186	8	6
10	n-PrCpTiCl$_3$	80	0.008	0.224	5	4

Reaction conditions: 3.0×10^{-6} mol catalyst; Al:Ti = 1000:1; 20 ml toluene solvent; 5 atm ethylene pressure; 30 min run time.

[a] In kg $(mol Ti)^{-1} h^{-1}$.
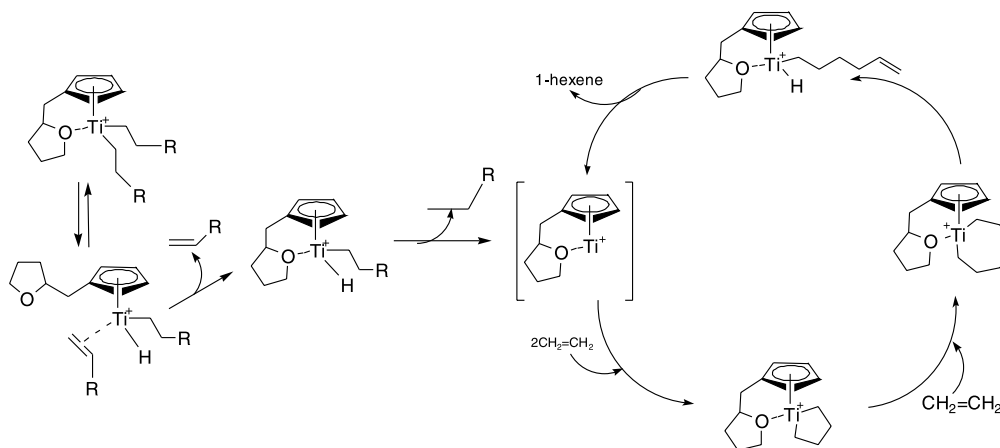
Scheme 2. Proposed mechanism for the formation of 1-hexene.

ethereal–cyclopentadienyl ligand exhibits hemilabile behavior, so **1**–**2**/MAO show activity for ethylene trimerization.

In complex **3**, the coordination of oxygen atom is not found in solid state. When complex **3** is activated by MAO, the oxygen could be coordinated to the generated cationic titanium center, and this coordination may be invariably labile in the temperature ranging from 30 to 80 °C, so **3**/MAO can selectively trimerize ethylene whether at room temperature or 80 °C.

Hessen proposed a mechanism involving metallacycle intermediates accouting for the selective formation of 1-hexene. By analogy, a possible mechanism proposed in our case is shown in Scheme 2 (exemplified for **2**/MAO catalyst system).

A titanium(II) species is generated initially from dialkyl titanium cationic species by β-H abstraction and reductive elimination. Hessen elucidated that the pendant arene may promote the formation of the titanium(II) species and provide additional stabilization to it. In our case, the coordination of ethereal group may also make the formation of the titanium(II) species much more favorable. This titanium (II) species reacts with two ethylene molecules to form a titanacyclopentane. A third molecule of ethylene inserts to form a titanacycloheptane. β-H abstraction from this species leads to the formation of a titanium(IV) alkylhydride. Reductive elimination regenerates titanium (II) and 1-hexene.

In summary, we have found that titanium complexes with an ethereal–pendant cyclopentadienyl ligand can selectively trimerize ethylene. The activity is moderate (25–57 kg (mol Ti)$^{-1}$ h^{-1}) and the selectivity is high (>90%). The pendant ethereal group is essential for the selective formation of 1-hexene. Better results will be obtained by regulating the electronic properties of the oxygen atom in the O-donors ligands.

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