

A Novel Method to Prepare a Metallocene Adduct Catalyst with Low Moisture Sensitivity

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ABSTRACT: A novel method to prepare a three-constituent adduct of metallocene $\text{Cp}_2\text{MCl}_2/2\text{LiCl}/\text{THF}$ is proposed. The adduct catalyst can be easily prepared without salt separation and recrystallization and possessed a low moisture sensitivity and a high stability. Measurements with NMR and XPS showed that specific intermolecular interactions exist among the three components, by which the stability of the adduct was increased. The activity of the cata-

lyst was evaluated in the polymerization of ethylene. The kinetic behavior was also studied. It showed a high reservation of activity even when exposed to a high relative humidity for hours. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3944–3948, 2006

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INTRODUCTION

Metallocene catalysts have received increasing attention because of their high activity in olefin polymerization and the controllability of the structure of the polymers produced by these catalysts.^{1–3} Generally, a process for synthesizing metallocene comprises converting cyclopentadiene or its derivative into an anion, complexing the resultant anion with a metal chloride, then separating and purifying the product to obtain a pure metallocene compound.

Lee and Diefenbach⁴ proposed a preparation procedure of (a) reacting $\text{Na}(\text{C}_5\text{H}_5)$ with RX (alkyl halide) in an organic solvent to form a mixture of RC_5H_4 and C_5H_5 ; (b) removing most of the C_5H_5 by vacuum stripping at room temperature; (c) protonating the RC_5H_4 , and (d) adding TiCl_4 or ZrCl_4 to form the metallocene compound, and then adding a solvent to separate out the pure metallocene compound.

Lisowsky⁵ proposed a process for preparing a transition metal complex compound having a mono-substituted cyclopentadiene ligand. The mono-substituted cyclopentadiene ligand is prepared by using an oxide or hydroxide of alkali metal or alkali earth metal as a protonating agent; then, the mono-substituted metallocene compound is formed by reacting the resultant ligand with a halide of transition metal elements.

Razavi⁶ suggested a process for preparing an isopropyl bridge-linked fluorenyl cyclopentadienyl zir-

conium dichloride. The process comprises two steps: (i) reacting butyl lithium or methyl lithium with a metallocene ligand in a polar solvent, e.g., tetrahydrofuran, then removing out the solvent to obtain a solid powder reactant; and (ii) reacting the solid powder reactant with ZrCl_4 powder at room temperature to carry out a solid–solid phase reaction in hexane, then removing out the solvent and washing the remainder to obtain a mixture of the isopropyl bridge-linked fluorenyl cyclopentadienyl zirconium dichloride and LiCl .

However, the aforementioned preparation methods of the metallocene catalysts have several common shortcomings: (i) multistep reactions are involved, resulting in poor control and low yields (around 60%); (ii) complicated separation and purification are needed in the preparation; and (iii) the stability of the metallocene compound in air is poor, especially at high relative humidities; therefore, it cannot be easily stored for a long time.

In this article, a novel method is proposed to prepare a three-constituent adduct of metallocene, cyclopentadienyl metal dichloride/lithium chloride/tetrahydrofuran ($\text{Cp}_2\text{MCl}_2/2\text{LiCl}/\text{THF}$). It can be easily prepared without salt separation and recrystallization and possesses a high air stability and a low moisture sensitivity. The activity of the catalyst was evaluated in the polymerization of ethylene.

EXPERIMENTAL

Materials

ZrCl_4 and TiCl_4 from Fluka, cyclopentadiene (AR), methyl cyclopentadiene (AR), *n*-BuLi (2.5 mol/L solu-

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TABLE I
Composition and Yield of the Adducts

Adducts	Content of Zr or Ti (wt %)	Content of Li (wt %)	Yield of Zr or Ti (wt %)	Yield of solid (wt %)
Cp ₂ TiCl ₂ /2LiCl/THF	10.91	5.31	19.63	88.4
(MeCp) ₂ TiCl ₂ /2LiCl/THF	9.87	4.68	17.78	80.1
(BuCp) ₂ TiCl ₂ /2LiCl/THF	9.05	4.08	18.58	86.2
Cp ₂ ZrCl ₂ /2LiCl/THF	19.92	4.4	19.26	92.9
(MeCp) ₂ ZrCl ₂ /2LiCl/THF	20.53	3.62	16.66	82.7
(BuCp) ₂ ZrCl ₂ /2LiCl/THF	19.63	3.10	18.57	87.5

tion in ether), from Adrich, MAO (10 wt % solution in toluene) from Albemarle were used as received. Nitrogen and ethylene were further purified before use by passing them through columns containing 4-Å molecular sieves and copper catalyst as oxygen scavenger. Toluene was purified by distillation over elemental sodium under nitrogen atmosphere to remove residual trace of moisture and oxygen.

Preparation and characterization

In a 250-mL three-neck flask in an ice bath, 11.0 g cyclopentadiene (with a substituent) was dissolved with 100 g tetrahydrofuran, into which a solution (40 mL) of butyl lithium in hexane (2.5M) was introduced dropwise, with stirring, protected with N₂. After the addition, the mixture was stirred under room temperature for two more hours to generate a white suspension. Subsequently, the flask was introduced into a dry ice-acetone bath, and 10 g of ZrCl₄ (or TiCl₄) powder was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 6 h to obtain a yellow suspension. The system was subsequently distilled at 35°C to remove tetrahydrofuran and washed with petroleum ether at 60–90°C for 2–5 h. A solid product was obtained after filtration and drying.

Two series of adducts were thus obtained based on Zr and Ti with different substituents on cyclopentadiene. The contents of Zr, Ti, and Li, the yields of Zr and Ti, and the solid yields are summarized in Table I.

TABLE II
Binding Energy of Various Elements in Different Compounds

Species	BE (eV)		
	Zr _{3d5/2}	Cl _{2p3/2}	Li
LiCl	–	198.5	56.0
Cp ₂ ZrCl ₂	181.7	199.6	–
Cp ₂ ZrCl ₂ /2LiCl/THF	183.3	200.2	57.5
Mixture	–	198.7	56.2
	181.8	200.3	–

The contents of Zr, Ti, and Li were determined using atomic emission spectroscopy (Varian Vistapro, America). Subliming point and binding energy were measured using X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, England).

¹H nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AV-600 NMR. The operating parameters for ¹H NMR were as follows: sweep width, 600 MHz; pulse width, 5.80 μs; number of scans, 16.

Moisture sensitivity evaluation

An adduct catalyst [(BuCp)₂ZrCl₂/LiCl/THF] was allowed to stand in air flows of different relative humidities for various lengths of time; subsequently, it was employed in the flask polymerization of ethylene and the activity was measured. The activity reservation relative to that of the fresh one was taken as a measure of the moisture sensitivity.

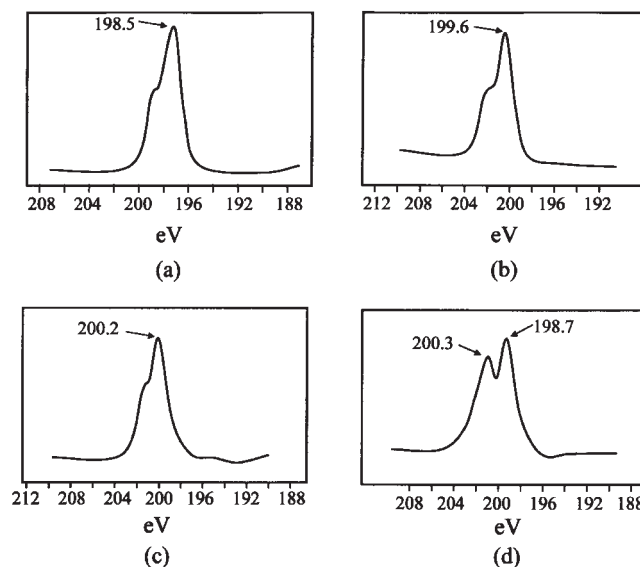


Figure 1 Cl_{2p3/2} binding energy: (a) LiCl, (b) Cp₂ZrCl₂, (c) Cp₂ZrCl₂/2LiCl/THF, and (d) mixture.

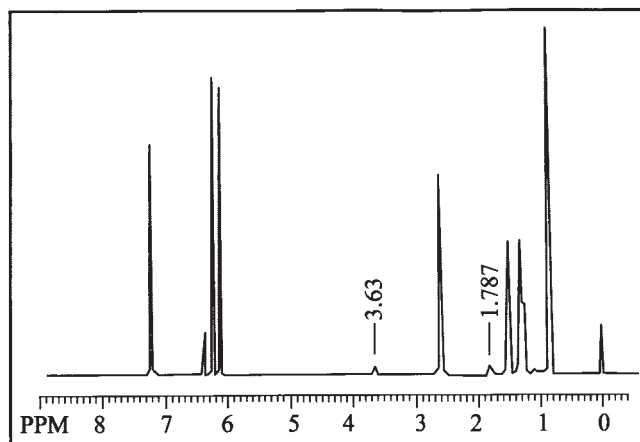


Figure 2 ^1H NMR spectrogram of the adduct $\text{Cp}_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$.

Polymerization in glass flask

A 250-mL glass flask equipped with a magnetic stirrer was purged with nitrogen and filled with ethylene, into which was subsequently introduced 100 mL of toluene and 2.56 mL of MAO solution. The system was maintained at 60°C . When the adsorption equilibrium of ethylene was achieved, 2- μmol metallocene catalyst was introduced with a syringe to initiate the polymerization, which was allowed to run for 1 h.

Polymerization in autoclave

A 1-L stainless autoclave was purged with nitrogen and subsequently the nitrogen was replaced with ethylene. A mixture of adduct catalyst, toluene, and MAO was introduced into the autoclave. The polymerization was carried out at 70°C , 0.7 MPa for 1 h.

RESULTS AND DISCUSSION

The binding energy of various species for different compounds is listed in Table II. Comparing the binding energies of LiCl and Cp_2ZrCl_2 with those of the mixture ($\text{Cp}_2\text{ZrCl}_2 + \text{LiCl}$), one may find the changes were within 1 eV. This indicated that neither chemical nor physical interactions occurred between the com-

ponents in the mixture. However, the binding energies of an adduct ($\text{Cp}_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$) were at least 1.5 eV larger than the corresponding ones of the neat component; thus, one may conclude that the components combined well with some interaction.

The $\text{Cl}_{2p3/2}$ binding energy peaks in Figure 1 present the interaction in the adduct more clearly. Figures 1(a) and 1(b) are the $\text{Cl}_{2p3/2}$ peaks for Cp_2ZrCl_2 and LiCl respectively. One may notice that the absorbency of the mixture [Fig. 1(c)] possessed two peaks, which appeared at the same position of neat Cp_2ZrCl_2 and LiCl respectively. In other words, the trace of the mixture was simply a superposition from those of its components. However, the trace of the adduct [Fig. 1(d)] exhibited only one peak. This means that the sample is not merely a mixture; its components were combined in some way into a complex, which could be denoted as $\text{Cp}_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$.

The sublimation behavior of LiCl, metallocene Cp_2ZrCl_2 , and the ternary adduct $\text{Cp}_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$ were also measured using XPS. The obtained subliming point of metallocene was $(150 \pm 0.5)^\circ\text{C}$, and no subliming of LiCl was observed below 1000°C . However, $\text{Cp}_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$ sublimed completely at $(175 \pm 0.5)^\circ\text{C}$, and no LiCl remained. This confirmed once more that the three components of the adduct combined into a whole entity.

Figure 2 is a spectrogram obtained by ^1H NMR of the structure of the adduct $\text{Cp}_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$. The characteristic peaks of the tetrahydrofuran, $\delta 1.787$ and $\delta 3.63$, can be obviously observed in the determination of the adduct structure by ^1H NMR, which is the evidence of the existence of the adduct according to this work.

Furthermore, when the adduct was extracted easily with a solvent to dissolve the metallocene adduct, such as methyl dichloride, the pure metallocene compound obtained by tile separation and recrystallization was extremely sensitive to air. However, the three-constituent adduct was not sensitive to air and could be exposed in air for several hours or stored in nitrogen gas for a long period of time, when it was not separated and recrystallized but being used directly as a three-component substance. All the characteristic results showed that intermolecular forces exist among

TABLE III
Conditions for and Results of Flask Polymerization^a

Catalyst	Amount of Zr (μmol)	Amount of MAO (mmol)	Al/Zr (mol/mol)	Activity (10^6 gPE/molZr h)
$\text{Cp}_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$	2	4	2000	1.25
$(\text{MeCp})_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$	2	4	2000	1.06
$(\text{BuCp})_2\text{ZrCl}_2/2\text{LiCl}/\text{THF}$	2	4	2000	1.26
Cp_2ZrCl_2	2	4	2000	0.8

^a Other conditions: 1 atm; 60°C ; 1 h; solvent, 100 mL of toluene.

TABLE IV
Conditions for and Results of Autoclave Polymerization

Catalyst	Amount of MAO (mmol)	Al/Zr or Al/Ti (mol/mol)	Activity (10^5 gPE/molM h)
$Cp_2TiCl_2/2LiCl/THF$	0.0776	500	3.0
$(MeCp)_2TiCl_2/2LiCl/THF$	0.1552	500	1.5
$(BuCp)_2TiCl_2/2LiCl/THF$	0.0776	500	1.3
$Cp_2ZrCl_2/2LiCl/THF$	0.0776	500	0.8
$(MeCp)_2ZrCl_2/2LiCl/THF$	0.0776	500	3.6
$(BuCp)_2ZrCl_2/2LiCl/THF$	0.0776	500	7.6
Cp_2ZrCl_2	0.0776	500	0.6

Polymerization conditions: 0.7 MPa; 70°C; stirring speed, 250 rpm, 1 h.

the three components in the said adduct, by which the stability of the adduct is increased.

Table III lists the conditions and the activity of the Zr series adduct in the flask polymerization. One may notice that at an Al/Zr ratio of 2000, a reasonably high activity of ethylene polymerization was achieved. Compared with metallocene Cp_2ZrCl_2 , the adducts exhibited a better performance.

Table IV shows a comparison of polymerization activities of the catalyst in autoclave with a low Al/Zr ratio (500/1). It showed that all the adduct catalysts possessed a higher activity than that of Cp_2ZrCl_2 , with the Zr series being better than Ti series. The superiority of Zr over Ti has also been reported in other literatures.^{7,8} It was worth noting that the substituent on the cyclopentadiene had a strong effect on the activity. It is interesting to notice that the effects in Zr and Ti series are in a contrary direction. In the Zr series, the larger the substituent, the higher the activity, i.e., $Bu \rightarrow Me \rightarrow H$; however, in the Ti series, the order is $H \rightarrow Me \rightarrow Bu$. A detailed under-

standing of the mechanism is unavailable; it must be originated from the particular electron structure.⁹

The kinetic behavior of the $(BuCp)_2ZrCl_2/2LiCl/THF$ catalyst is presented in Figure 3 (squares). The activity increased sharply at the first 10 min and gave rise to a maximum of about 4×10^7 gPE/molZr h. Subsequently, the activity decreased rapidly and stabilized at level about 5×10^6 gPE/molZr h after 40 min. This behavior was comparable with that of a traditional metallocene catalyst $(BuCp)_2ZrCl_2$ (circles).

The moisture sensitivity of the $(BuCp)_2ZrCl_2/2LiCl/THF$ catalyst after standing in both dry (RH = 25%) (Table V) and wet (RH = 75%) air (Table VI) was compared with that of $(BuCp)_2ZrCl_2$. The initial activities of the two catalysts were comparable; however, the deactivating rates were quite different. After 72 h of standing in dry air, the reservation of activities was 51% for $(BuCp)_2ZrCl_2/2LiCl/THF$ and 39% for $(BuCp)_2ZrCl_2$. In the wet air, a sharp contrast was noticed. With 2 h of standing, the activity reservation for $(BuCp)_2ZrCl_2/2LiCl/THF$ was 81% when compared with the 42% for $(BuCp)_2ZrCl_2$. After 4 h of standing, the $(BuCp)_2ZrCl_2/2LiCl/THF$ showed an activity reservation of 69%, which is reasonably high, while the $(BuCp)_2ZrCl_2$ was deactivated almost completely. The presence of THF in the adduct was probably responsible for its low moisture sensitivity. THF was expected to coordinate with the central atom or

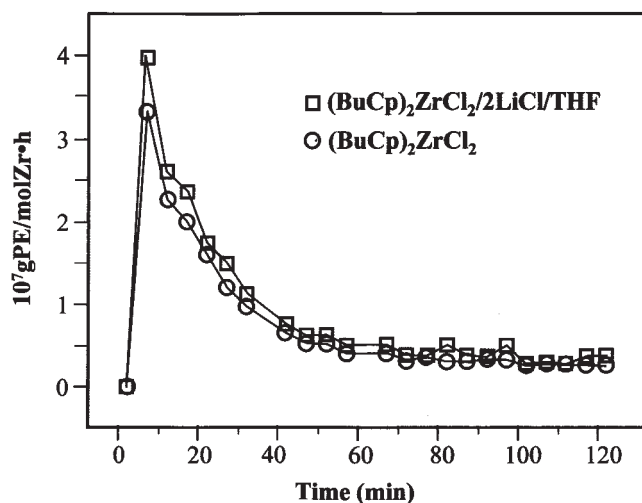


Figure 3 The kinetic behavior of an adduct and a traditional catalyst. Polymerization conditions: 1 atm; 60°C; Al/Zr, 2000.

TABLE V
Polymerization Activities after Standing in Dry Air (RH = 25%)

Catalyst	Polymerization activity (10^6 gPE/molZr h)		
	0 ^a	24	72
$(BuCp)_2ZrCl_2/2LiCl/THF$	3.12	3.05	1.6
$(BuCp)_2ZrCl_2$	3.07	2.96	1.2

Catalyst loading, 2.2 μ mol; MAO, 2.2 mmol in 500 mL hexane; polymerization temperature, 50°C; pressure, 0.1 MPa, for 1 hr.

^a 0, 24, and 72 are the standing time (in hours).

TABLE VI
Polymerization Activities after Standing in Wet Air
(RH = 75%)

Catalyst	Polymerization activity (10 ⁶ gPE/molZr h)			
	0 ^a	2	4	24
(BuCp) ₂ ZrCl ₂ /2LiCl/THF	3.12	2.54	2.15	0.47
(BuCp) ₂ ZrCl ₂	3.07	1.3	0.26	0

Catalyst loading, 2.2 μmol; MAO, 2.2 mmol in 500 mL hexane; polymerization temperature, 50°C; pressure, 0.1 MPa, for 1hr.

^a 0, 2, 4, 24 are the standing time (in hours).

with lithium that was coordinated with chloride and thus stabilized the central atoms.

CONCLUSIONS

A three-constituent adduct was prepared without salt separation and recrystallization with a high yield. Spe-

cific intermolecular interactions among the three components of the adduct combined the adduct into a stable structure, which resulted in a high stability during the polymerization of ethylene and a low moisture sensitivity during the storage.

References

1. Kaminsky, W.; Sinn, H. *Adv Organomet Chem* 1980, 18, 99.
2. Cho, H. S.; Chung, J. S.; Han, J. H.; Ko, Y. G.; Lee, W. Y. *J Appl Polym Sci* 1998, 70, 1707.
3. Yoon, J. S.; Oh, J. K.; Hong, K. P.; Lee, I. M. *Korean J Chem Eng* 1996, 13, 207.
4. Lee, J. Y.; Diefenbach, S. P. US Pat. 5,200,537.
5. Lisowsky, R. US Pat. 5,336,795.
6. Razavi, A. Eur. Pat. 426643 (1991).
7. Moehring, P. C.; Coville, N. J. *J Mol Catal A: Chem* 1995, 96, 181.
8. Bochmann, M. *J Chem Soc Dalton Trans* 1996, 3, 255.
9. Tait, P. J. T.; Booth, B. L.; Jejelowo, M. O. *ACS Symp Ser* 1992, 496, 78.