Communications

Synthesis of Titanium(IV) Complexes with Schiff-base Ligand and Their Catalytic Activities for Polymerization of Ethylene and Styrene

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Reaction of titanium(IV) isopropoxide with the unusual kind of Shiff-base in 1:1 molar ratio gives a variety of new derivatives of titanium(IV) in high yield. These complexes were characterized by elemental analyses, IR, MS and ^{1}H NMR. It was noteworthy to find that all these complexes were active for polymerizations of ethylene and styrene when activated by a Lewis acid cocatalyst (MAO).

Keywords   Schiff-base, catalytic activities, syndiotactic polymerization of styrene, polymerization of ethylene

Introduction

Discovery of Ziegler-Natta catalyst makes chemists devote themselves to exploring group 4 olefin polymerization catalyst precursors, such as Cp_2MX_2, $CpMX_3$, and linked Cp-amide derivatives.[1,2] Although organotitanium complexes with cyclopentadienyl-type spectator ligands have been studied extensively, complexes with non-cyclopentadienyl ligand remain relatively unexplored.[3-11] In recent years, a new trend has been the incorporation of non-cyclopentadienyl ancillary ligands. Such interest has, in part, stemmed from the principal that the coordination sphere of such catalysts might be more easily tuned by using non-cyclopentadienyl based ligands.

Among the non-cyclopentadienyl ligands studied, the tetradentate Schiff-base ligand recently draw much attention not only for their easy access and tunable structural feature, but also for their steric and electronic properties—incorporation of two oxygen functions which decrease the electron donor ability and increase the metal electrophilicity in the resulting complexes.[12,13] Schiff-base ligands have been used throughout the transition metal series.[14] Many chemists synthesized the structures of (acen)TiCl$_2$, (salen)TiCl$_2$ and (salophen)TiCl$_2$, and studied their catalytic capabilities.[15-20]

To the best of our knoweledge, the diamides used in the Schiff-base ligand up to now were limited to α,β-diamide, but the Schiff-base ligand of m-diaminebenzene has not been studied. In this paper, we report the preparation and characterization of titanium(IV) complexes with such schiff-base ligands and their catalytic properties. It is interesting to find that these complexes are active for polymerization of both ethylene and styrene. But all other titanium(IV) complexes with Schiff-base ligand reported in literature have no or little catalytic activity for the polymerization of α-olefin.

Experimental

Materials and purification

All operations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried and purified by known procedures and distilled from benzophenone ketyl under argon prior to use. Methylaluminoxane (MAO) was purchased from BASF

and other chemicals were from Aldrich. Styrene was distilled from CaH_2.

Polymerization and measurements

Styrene polymerization was carried out in toluene in 250 mL crown-capped glass pressure reactors equipped with magnetic stirring and thermostated to the desired temperature. Ethylene polymerization was performed in a three-necked-flask in nitrogen atmosphere. DSC was performed on a Perkin-Elmer Thermal System IV.

Results and discussion

Synthesis of symmetrically disubstituted titanium (IV) complexes with Schiff-base ligand

Symmetrically disubstituted four-coordinate titanium(IV) complexes can be synthesized directly by the addition of $Ti(OPr^i)_4$ to H_2saphlen in toluene in good yield (Scheme 1). Complexes **2** are obtained as yellow to orange-red solid, and they are soluble and stable in organic solvents (*e.g.* toluene, CH_2Cl_2, CH_3CN, and

THF), allowing for full characterization by EA, IR, MS, and ^1H NMR spectroscopy. The infrared spectra of the titanium(IV) derivatives and the ligands indicate coordination of the ligands through azomethine nitrogen and phenolic oxygen as revealed.

Using complexes **2a—i** as α-olefin catalysts, their catalytic potential have been studied. As shown in Table 1, the catalytic activity of these complexes was moderate for ethylene polymerization. All the polymer obtained using **2a—i** have branched-structure. The substituent on ligands do effect the catalytic activity of the complexes, among these complexes the activity of **2b** was the lowest. This can be reasonalized by that the oxygen atom (OCH_3 group) in complex might consume some methylaluminoxane (MAO) and resulted in the decrease of the concentration of MAO that really takes part in the catalytic process.

The results of styrene polymerization were shown in Table 2. The yield of syndiotactic polystyrene (s-PS) (weight% product remaining after 2-butanone extraction) was from moderate to high, being a maxium in Entry 2 (99%). It can be seen from Table 2, the catalytic activity increased when the ratio of Al/Ti increased from

Scheme 1
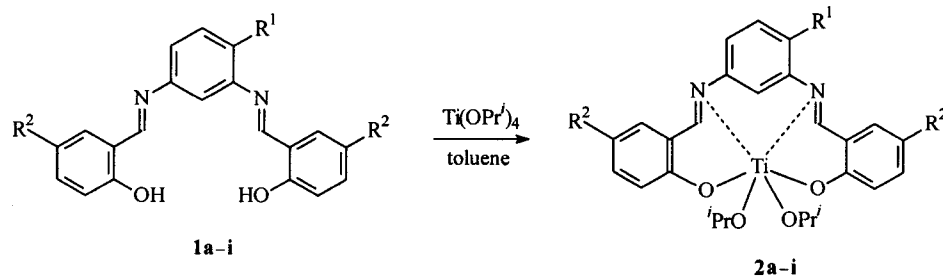
a: $R^1 = H$, $R^2 = H$;   b: $R^1 = H$, $R^2 = OCH_3$;   c: $R^1 = H$, $R^2 = Br$;   d: $R^1 = CH_3$, $R^2 = OCH_3$;   e: $R^1 = CH_3$, $R^2 = H$;
f: $R^1 = CH_3$, $R^2 = Br$;   g: $R^1 = CH_3$, $R^2 = t$-Bu;   h: $R^1 = H$, $R^2 = CH_3$;   i: $R^1 = H$, $R^2 = Cl$

Table 1   Ethylene polymerization catalyzed by complexes **2a—i**/MAO system ^{a}

Entry	Catalyst	Cat. (mg)	$x_{Al/Ti}$	Yield of PE (mg)	Activity(g/mol·Ti·h)
1	**2a** ($R^1 = H$, $R^2 = H$)	2.26	1500:1	47.9	2.04×10^4
2	**2b** ($R^1 = H$, $R^2 = OCH_3$)	2.95	1500:1	16.1	0.59×10^4
3	**2c** ($R^1 = H$, $R^2 = Br$)	3.20	1000:1	31.2	1.98×10^4
4	**2d** ($R^1 = CH_3$, $R^2 = OCH_3$)	2.71	1000:1	20.7	0.85×10^4
5	**2e** ($R^1 = CH_3$, $R^2 = H$)	2.47	1000:1	24.4	0.98×10^4
6	**2f** ($R^1 = CH_3$, $R^2 = Br$)	3.24	1500:1	98.2	3.94×10^4
7	**2g** ($R^1 = H$, $R^2 = t$-Bu)	2.00	1500:1	29.2	1.73×10^4
8	**2h** ($R^1 = H$, $R^2 = CH_3$)	2.54	1500:1	21.9	0.84×10^4
9	**2i** ($R^1 = H$, $R^2 = Cl$)	2.745	1500:1	25.3	1.00×10^4
Ref.	Cp_2TiCl_2	1.195	1500:1	746.6	3.11×10^5

^{a} Polymerization condition: $c_{Al} = 1.44$ mol/L; $T_p = 50℃$; Solvent: toluene; Time: 0.5 h.

2000 to 4000, which agrees with those reported by Ishi-hara,[21] Kaminsky,[22] Chien[23] and Ewen.[24] The substitution on the ligand affects the catalytic activity slightly, all these four new complexes showed similar activity for the syndiotactic polymerization of styrene. But the substitution on the ligand affects the s-PS% greatly. The activity of complexes 2a—c, 2e was lower than that found for CpTiCl$_3$, but the syndiospecificity in Entry 2 (99.2%) was little higher than that for CpTiCl$_3$. The melting points of polystyrene obtained using complex

2a—c, 2e were 269.05—271.95℃.

In Table 3, Styrene was polymerized in bulk. It can be seen from Table 3, the catalytic activities of these four complexes were satisfied comparing to the catalytic activity in Table 2, the catalytic activities of these four complexes reached 105 g of PS/(molTi·molS·h). It is satisfactory in no-Cp titanium complexes. The catalytic activity increased when the temperature increased from 25℃ to 90℃.

Table 2 Syndiotactic polymerization of styrene catalyzed by complexes 2a—c, 2e/MAO system [a]

Entry	Catalyst	c_{Ti} (mmol/L)	$x_{Al/Ti}$ ($\times 10^3$)	Time (h)	Yield of PS (mg)	A^b ($\times 10^4$)	s-PS^c (%)	T_{mp} (℃)
1	**2a**	0.42	2.0	24	25.4	1.21	58.3	269.05
	R^1 = H, R^2 = H	0.21	4.0	24	23.6	2.26	70.3	–
2	**2b**	0.42	2.0	24	21.1	1.01	50.7	271.06
	R^1 = H, R^2 = OCH$_3$	0.21	4.0	24	12.5	1.20	99.2	–
3	**2c**	0.42	2.0	24	21.3	1.02	86.8	271.59
	R^1 = H, R^2 = Br	0.21	4.0	24	17.9	1.71	84.4	–
4	**2e**	0.42	2.0	24	27.9	1.34	79.2	271.95
	R^1 = CH$_3$, R^2 = H	0.21	4.0	24	20.9	2.00	75.6	–
5	CpTiCl$_3$	0.42	2.0	1	313	360	96.3	–
6	CpTiCl$_2$(OPr^i)	0.42	2.0	1	324	372	97.2	–

[a] Polymerization condition: 2 mL of styrene, c_{Al} = 0.83 mol/L, c_S = 1.45 mol/L, T_p = 50℃; [b] g of PS/(molTi·molS·h);
[c] weight% of s-PS insoluble in refluxing 2-butanone.

Table 3 Syndiotactic polymerization of styrene catalyzed by complexes 2a—c, 2e/MAO system [a]

Entry	Complexes	c_{Ti} (mmol/L)	$x_{Al/Ti}$ (mol/mol)	Temp. (℃)	Time (h)	A^b ($\times 10^5$)	s-PS^c (%)
1	**2a**	0.42	300	50	4	1.42	33.0
	R^1 = H, R^2 = H	0.42	300	70	1.5	3.75	57.8
		0.42	300	90	3	3.85	61.4
		0.42	300	25	15	2.54	36.1
2	**2b**	0.42	300	50	3.67	1.61	49.6
		0.42	300	70	4	3.12	55.6
	(R^1 = H, R^2 = OCH$_3$)	0.42	300	90	6	3.14	68.6
		0.42	300	25	7	0.39	17.5
3	**2c**	0.42	300	50	3.67	1.53	59.9
	(R^1 = H, R^2 = Br)	0.42	300	70	4	2.48	62.2
		0.42	300	90	6	2.99	75.6
		0.42	300	25	7	0.37	34.2
4	**2e**	0.42	300	50	3.67	2.23	72.2
	(R^1 = CH$_3$, R^2 = H)	0.42	300	70	4	3.15	80.1
		0.42	300	90	6	3.29	77.4
		0.42	300	25	7	0.39	65.2
5	CpTiCl$_3$	0.42	300	70	1	32.9	73.1
		0.42	300	90	2	21.3	72.4
		0.42	300	25	0.5	22	32.3

[a] Polymerization condition: 11 mL of styrene, no addition solvent, c_{Al} = 0.125 mol/L, c_S = 7.97 mol/L; [b] g of PS/(molTi·molS·h);
[c] weight % of s-PS insoluble in refluxing 2-butanone.

References

1   Devore, D. D.; Timmers, F. J.; Hasha, D. L. *Organometallics* **1995**, *14*, 3132.

2   Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

3   Tsuie, B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 1392.

4   Bailich, G.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc*. **1993**, *115*, 1581.

5   Schollard, J. D.; McConville, N. C.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.

6   Tjaden, E. B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1995**, *14*, 371.

7   Giannini, L.; Floriani, C.; Chiesi-Villa, A. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 2204.

8   Jacoby, D.; Isoz, S.; Floriani, C.; Chiesi-Villa, A. *J. Am. Chem. Soc*. **1995**, *117*, 2793.

9   Brand, H.; Arnold, J. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 95.

10   Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc*. **1996**, *118*, 10008.

11   Holm, R. H.; Everett, G. W.; Chakravorty, A. *Prog. Inorg. Chem*. **1996**, *7*, 83.

12   Jacobsen, E. N.; Zhang, W. *J. Am. Chem. Soc*. **1990**, *112*, 2801.

13   Cobrazza, F.; Solari, E.; Floriani, C. *J. Chem. Soc., Dalton Trans*. **1990**, 1335.

14   Vander Velde, S. L.; Jacobsen, E. N. *J. Org. Chem*. **1995**, *60*, 5380.

15   Fukuda, T.; Katsuki, L. *Tetrahedron* **1997**, *53*, 7201.

16   Du Bois, J.; Tomooka, C. S.; Hong, J. *Acc. Chem. Res*. **1997**, *30*, 364.

17   Fukuda, T.; Katsuki, T. *Tetrahedron Lett*. **1997**, *38*, 3435.

18   Schaus, S. E.; Branalt, J.; Jacobsen, E. N. *J. Org. Chem*. **1998**, *63*, 403.

19   Irie, R.; Katsuki, L. *Tetrahedron Lett*. **1996**, *37*, 4979.

20   Jacobsen, E. N.; Kakiuchi, F.; Konsler, R. G. *Tetrahedron Lett*. **1997**, *38*, 773.

21   Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356.

22   Kaminsky, W.; Miri, M.; Sinn, H. *Makromol. Chem., Rapid Commun*. **1983**, *4*, 417.

23   Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci., Part A: Polym. Chem*. **1988**, *26*, 3089.

24   Ewen, J. A. *J. Am. Chem. Soc*. **1984**, *106*, 6355.

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