Note

Synthesis, characterization, and catalytic behaviors of β-carbonylenamine-derived metal complexes (M = Ti, Zr) in styrene polymerization

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ABSTRACT

The titanium and zirconium complexes based on thioether substituted β-carbonylenamine were prepared and characterized. In the presence of MMAO, the titanium complexes showed good activity in syndiospecific styrene polymerization with high syndioselectivity, and performed good thermal stability. Electron withdrawing group on ligands is beneficial to the styrene polymerization. [1,3-diphenyl-3-(2-(isopropylthio)ethylimino)prop-1-en-1-olate]$_2$ZrCl$_2$(IV) could also polymerize styrene to give syndiotactic polymer, however in low activity and with low syndioselectivity.

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Introduction

Developing group IV metal complexes and revealing their catalytic behaviors in homogeneous polymerizations have attracted much attention in academic as well as in industrial fields [1,2]. Up to now, fruitful reports have been known in regard to the metal complexes and their catalytic behaviors [1–3]. For example, scientists in The Dow Chemical Company produced olefin block copolymers with alternating semicrystalline and amorphous segments by combining a zirconium bis(phenoxyimine) complex and a hafnium pyridylamide complex [2b]. Fujita et al. revealed that bis(phenoxy-imine) Ti complexes (Ti-FI catalysts) combined with dried MAO (DMAO) showed unique styrene polymerization behavior, and an iPS/sPS mixture can be produced using fluorinated Ti-FI catalysts [3a]. We have developed series of titanium complexes and investigated their properties in catalyzing olefin polymerization [4]. It was envisioned that a pendant coordination group in ligand could act as a controller of the environmental and electronic properties of the catalytic site to tune the catalytic behaviors.

In the presence of MMAO, the titanium complexes based on thioether substituted β-carbonylenamine displayed versatile catalytic behaviors for the (co)polymerization of ethylene with comonomers including α-olefins and cycloolefins [4d]. In addition, good tolerance to functional groups permits the titanium complexes to be applied in the ethylene/polar olefins copolymerization. As a result, ω-alkenol, ω-alkenoic acid, and ω-alkenoic ester were incorporated into PE backbone in high activity and good incorporation [4c,g]. Since styrene polymerization stereoselectively is important [3], very recently, we further investigated the behaviors of the titanium complexes in styrene polymerization. We found that the complexes performed high activity in syndiospecific styrene polymerization. The complexes were stable enough to promote the styrene polymerization for at least 4 h at 90 °C. Bis(β-carbonylenamine) zirconium dichloride was obtained for the first time, however, gave only low activity and poor syndiotacticity. In this contribution, we provide details for the synthesis, characterization and reactivity of the complexes.

Experimental

General considerations

All air or moisture sensitive manipulations were carried out under nitrogen atmosphere using Schlenk techniques. ^{1}H NMR, ^{13}C

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NMR spectra were recorded on Varian Mercury 300 spectrometer and Varian 400 MR spectrometer. Mass spectra were carried out with a HP5989A spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). M_n, M_w, and M_w/M_n values of polymers were determined with a waters Alliance GPC 2000 series at 135 °C (polystyrene calibration, 1,2,4-trichlorobenzene as a solvent at a flow rate of 0.92 mL min^{-1}). ^{13}C NMR date of polymer was obtained using o-dichlorobenzene-d_4 as a solvent at 110 °C. X-Ray crystallographic data were collected using a Bruker AXSD8 X-ray diffractometer. Toluene, hexane, CH_2Cl_2 (DCM) and THF solutions were purified by MB SPS-800 system. Modified methylaluminoxane (MMAO-3A) was purchased from Akzo Chemical as a 1.88 M heptane solution. Polymerization-grade ethylene was purified before use. The complexes **2** were prepared according to the literature methods [4c,d,g].

The synthesis of complexes bis[1,3-diphenyl-3-(2-(isopropylthio) ethylimino)prop-1-en-1-olate]Zr(IV) dichloride (**3**)

To a suspension of potassium hydride (KH) (0.37 g, 9.4 mmol) in THF (20 mL) was added a solution of **1b** (2.4 g, 7.5 mmol) in THF (10 mL) at −78 °C. The resulting suspension was warmed to room temperature and stirred for 3 h. After removal of the solvent under vacuum, toluene (20 mL) was added to the residue to give a yellow solution. It was then added dropwise to a solution of $ZrCl_4$ (0.87 g, 3.7 mmol) in toluene (30 mL) at −78 °C, and the mixture was stirred for 14 h. The solution was concentrated under vacuum and crystallized at −30 °C to give complex **3** as a yellow crystal. Yield: 2.1 g (70%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.96 (d, J = 6.9 Hz, 4H, Ph–H), 7.23–7.47 (m, 16H, Ph–H), 6.28 (s, 2H, CHCO), 3.73 (t, J = 8.1 Hz, 4H, CH_2N), 2.55 (br s, 4H, SCH_2), 2.40–2.34 (m, 2H, SCH), 0.93 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 175.7, 167.9 138.8, 134.5, 131.5, 129.2, 128.9, 128.6, 127.3, 126.1, 104.6, 53.2, 34.6, 29.8, 23.4. C$_{40}$H$_{44}$Cl$_2$N$_2$O$_2$S$_2$Zr (811.05): calcd C 59.24, H 5.47, N 3.45. Found C 59.43, H 5.59, N 3.45.

Typical procedure for styrene polymerization

To a solution of catalyst (1 mL, 3 μmol/mol in toluene) in styrene (20 mL) was added a solution of MMAO (4.8 mL, 1.88 M in heptane) at 90 °C. After the desired reaction time, the polymerization was quenched with concentrated HCl in ethanol (400 mL, HCl/EtOH, 1/20, v/v). The precipitated polymer was collected, washed with ethanol, and then dried overnight in a vacuum oven at 60 °C to constant weight. The polymer was extracted with refluxing 2-butanone for 4 h in order to determine the sPS portion of the polymer obtain.

X-ray structure determination

All single crystals were sealed under N$_2$ in thin-walled glass capillaries. Data were collected at 293 K on a Bruker AXSD8 X-ray diffractometer using Mo K radiation. An empirical absorption correction was applied using the SADABS program [5]. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package (PC version) [6]. All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements were given in Table 1. Further details were included in the Supporting information.

Table 1
Summary of data collection and refinement details for **2c** and **3**.

|	**2c**	**3**
Formula	C$_{15}$H$_{20}$Cl$_3$NOSTi	C$_{54}$H$_{58}$N$_2$O$_2$S$_2$Zr
fw	416.63	922.36
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)
a, Å	7.830(4)	14.4191(6)
b, Å	12.021(6)	11.9417(5)
c, Å	19.930(10)	14.7669(6)
α, deg	90	90
β, deg	95.954(10)	110.8570(10)
γ, deg	90	90
V, Å^3	1865.8(16)	2376.07(17)
Z	4	2
D_{calcd}, Mg/m^3	1.483	1.289
2θ range, deg	3.96–51.0	3.02–50.02
$F(000)$	856	968
Reflections collected/unique	9476/3477	27,449/8226
Goodness-of-fit on F^2	0.812	1.064
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Completeness to theta = 25.50	0.998	0.999
$R1$	0.0783	0.0230
$wR2$	0.1628	0.0602

Result and discussion

Synthesis of the ligands and complexes

Both ligands **1** and complexes **2** were synthesized in good to high yields according to the reported procedures [4c,d,g] (Scheme 1). The red single crystal of complex **2c** suitable for X-ray diffraction was grown in toluene at room temperature. As shown in Fig. 1, the molecular structure of **2c** adopts a distorted octahedral geometry, in which titanium is coordinated by enolate oxygen, imine nitrogen, sulfur atom and three chlorides. Three chlorides occupy the *mer* position. Bond length of C3−O1 indicates its single bond character (1.323(10) Å), while C1−N1 bond lengths (1.324(11) Å) reveals some double bond nature. The bond angles of Cl1−Ti−Cl2, Cl2−Ti−Cl3 and Cl1−Ti−Cl3 are 91.74(12), 92.82(12) and 168.20(13), respectively. This orientation is favorable for the olefin coordination and insertion. The bond angles of C13−S−C12, C13−S−Ti, and C12−S−Ti in complex **2c** are 102.8(5), 112.5(3), and 96.2(3), respectively. The bond angle sum around S atom (311.5°) suggests that the sulfur atom in complex **2c** is sp^3-hybridized.
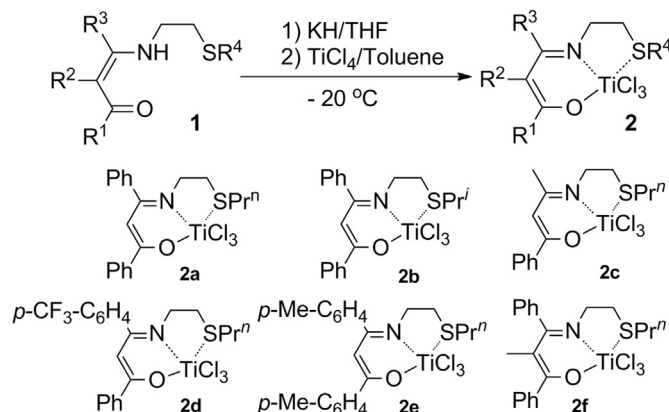
Scheme 1. Synthesis of titanium complexes **2**.
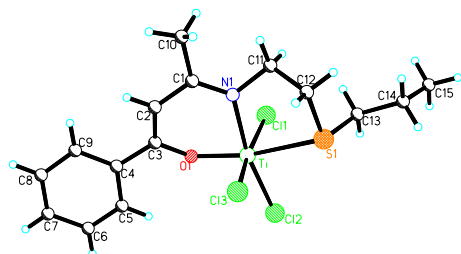
Fig. 1. ORTEP drawing of Ti complex **2c**. Selected bond lengths (Å) and bond angles (deg): Ti–O1 = 1.830(6), Ti–N1 = 2.175(8), Ti–S = 2.609(3), O1–C3 = 1.323(10), C2–C3 = 1.354(13), C1–C2 = 1.432(13), N1–C1 = 1.324(11), Ti–S1 = 2.609; ∠Cl2–Ti–Cl3 = 92.82(12), ∠Cl2–Ti–Cl1 = 91.74(12), ∠Cl3–Ti–Cl1 = 168.20(13), ∠C12–S–C13 = 102.8(5), ∠C13–S–Ti = 112.5(3), ∠C12–S–Ti = 96.2(3).

We tried to synthesize the zirconium analog under similar conditions (Scheme 2). However only bis[1,3-diphenyl-3-(2-(iso-propylthio)ethylimino)prop-1-en-1-olate] Zr(IV) dichloride **3** could be separated after **1b** was treated with ZrCl$_4$, no matter the **1b**/ZrCl$_4$ molar ratio being 1/1 or 2/1.

The structure of **3** was determined by ^{1}H NMR and ^{13}C NMR. Comparing to the corresponding titanium complex **2b** [4d], the signal of =CH in enolate fragment moves from 6.40 to 6.29 ppm. Both ^{1}H NMR and ^{13}C NMR signals of –CH$_2$N and –CH$_2$S move upfield obviously. For example, variations of 0.47 ppm and 1.5 ppm respectively in ^{1}H NMR, and 4.2 and 7.6 ppm respectively in ^{13}C NMR are observed, indicating the electron rich nature in complex **3**. Fortunately, crystal of complex **3** suitable for X-ray analysis was collected from THF solution. As shown in Fig. 2, X-ray crystallographic analysis of **3** revealed that two ligands coordinated zirconium atom with enolate oxygen and imine nitrogen. No interaction between thioether groups and central metal exists. The bond lengths of O1–C3, C1–N1 are 1.318 (3) and 1.316 (4), respectively, similar to those of titanium complex **2c**. Two oxygen atoms are situated in trans-position (the angle of O1–Zr–O2 is 154.52(8)). Alternatively, two nitrogen atoms and the two chlorine atoms occupy cis-position (N1–Zr–N2, 85.89(9); Cl1–Zr–Cl2, 94.72(40)).

Styrene polymerization studies

Complex **2a** was first selected as a model to promote the styrene polymerization under various conditions. Since MMAO was supposed to initiate styrene atactic polymerization, blank polymerization was carried out first only in the presence of MMAO under the same polymerization conditions to preclude its influence.

The polymer produced in the presence of **2a**/MMAO was extracted with refluxing 2-butanone (MEK) for 4 h to separate the polymer into two parts. The MEK-soluble polymer is atactic PS according to its ^{13}C NMR spectroscopy. It was found that the weight of the resulting aPS increased with the improvement of polymerization temperature in the presence of **2a**/MMAO. However, its amount was always lower than that generated in the absence of **2a**,
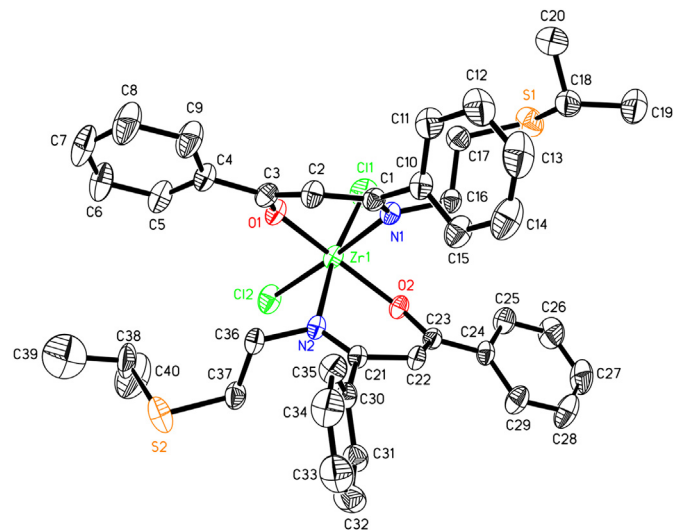
Fig. 2. ORTEP drawing of zirconium complex **3**. Selected bond lengths (Å) and bond angles (deg): Zr–O1 = 2.011(2), Zr–O2 = 2.0106(19), Zr–N1 = 2.289(3), Zr–N2 = 2.306(3), Zr–Cl1 = 2.4213(10), Zr–Cl2 = 2.4276(10), O1–C3 = 1.318(3), O2–C23 = 1.319(3), N1–C1 = 1.316(4), N2–C36 = 1.309; ∠O1–Zr–O2 = 154.52(8), ∠N1–Zr–Cl2 = 173.55(7), ∠N2–Zr–Cl1 = 171.13(6), ∠Cl1–Zr–Cl2 = 94.72(4), ∠N1–Zr–N2 = 85.89(9).

suggesting that the MEK-soluble portion produced in reaction system was mainly produced by MMAO. [3a,4h]

^{13}C NMR spectroscopy of the 2-butanone insoluble polymer exhibits a single sharp resonance at 145.2 ppm, which is a typical signal for the phenyl ipso carbon atom of the highly syndiotactic polystyrene [7], demonstrated that complex **2a** produced syndiotactic polystyrene selectively upon activation with MMAO. When the polymerization was carried out at 80 °C in the presence of **2a** and MMAO (Al/Ti 1500) for 20 min, sPS could be separated in an activity of 5.5×10^4 g sPS/mol h (entry 1, Table 2). The polymerization activity rose when further improving the polymerization temperature to 100 °C (6.0×10^4 g sPS/mol h). The molecular weight of the resulting sPS decreased with the improving of reaction temperature, probably owing to the increased chain-transfer rate. Under the circumstances, narrow molecular weight distribution (PDI 1.5–1.9) was observed.

The cocatalyst/catalyst molar ratio (Al/Ti ratio) had a strong influence on the catalytic activity. As shown in Table 3, only trace amount of polymer was obtained when **2a** was used at 90 °C with 500 Al/Ti ratio (entry 1). Enhancing Al/Ti ratio increased activity (entries 1–5). When the Al/Ti was 3000, the activity was increased to 8.6×10^4 g sPS/mol h (entry 5). Low catalyst loading was beneficial to the polymerization since too viscous polymerization system hampered the contact of monomer with active species (entries 5, 6). Notably the complex **2a** showed good stability. Prolonging the polymerization time had little influence on the activity (entries 6–12), and we found that the activity maintained even

Scheme 2. Synthesis of zirconium complex **3**.

Table 2
Effect of polymerization temperature.[a]

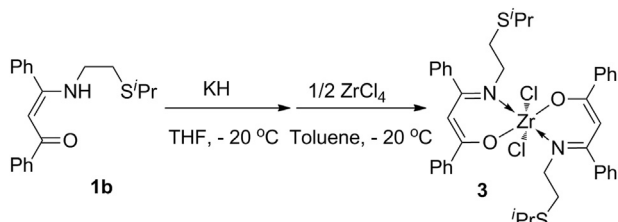| Entry	T (°C)	W_{sPS} (g)	W_{aPS} (g)	A[b]	M_n[c,d]	PDI[c]	W_{aPs}[e] (g)
1	80	0.1846	0.0433	5.5	8.4	1.5	0.0481
2	90	0.1948	0.0456	5.8	6.3	1.6	0.0713
3	100	0.2007	0.0633	6.0	2.7	1.9	0.1240

[a] Styrene (20 mL), **2a**: 10 μmol, MMAO/Ti = 1500, t = 20 min. W_{sPS}: weight of MEK-insoluble polymer; W_{aPS}: MEK-soluble polymer.
[b] The activity of sPS, 10^4 g sPS/mol h.
[c] Determined by GPC.
[d] 10^4 g/mol.
[e] Polymer generated only in the presence of MMAO (blank polymerization).

Table 3
Effect of other polymerization conditions.[a]

Entry	Al/Ti	Time (min)	W_{sPS} (g)	A[b]	M_n[c,d]	PDI[c]
1	500	20	Trace	–	–	–
2	1000	20	0.1588	4.8	4.4	2.0
3	1500	20	0.1945	5.8	6.3	1.6
4	2000	20	0.2057	6.2	4.2	1.9
5	3000	20	0.2873	8.6	4.6	1.9
6[e]	3000	20	0.1510	15	5.3	2.0
7[e]	3000	40	0.3063	14	4.9	1.9
8[e]	3000	120	0.7523	12	5.6	1.8
9[e]	3000	180	1.0397	12	3.7	2.2
10[e]	3000	240	1.3075	11	4.3	2.1

[a] Styrene: 20 mL, **2a**: 10 μmol, T: 90 °C.
[b] The activity of sPS, 10^4 g sPS/mol h.
[c] Determined by GPC.
[d] 10^4 g/mol.
[e] **2a**: 3 μmol.

Table 4
Syndiospecific polymerization results of styrene using **2**, **3**.[a]

Entry	Complex	A[b]	M_n[c,d]	PDI[d]	sPS(%)[e]
1	**2a**	1.5	5.3	2.0	>99
2	**2b**	1.8	2.6	2.1	>99
3	**2c**	1.3	2.5	3.2	>99
4	**2d**	1.7	5.2	1.9	>99
5	**2e**	1.3	5.7	2.0	>99
6	**2f**	0.6	8.2	2.6	34
7	**3**	0.2	4.4	3.3	73

[a] Styrene: 20 mL, complex: 3 μmol, MMAO/Ti = 3000, T = 90 °C, t = 20 min.
[b] The activity of sPS, 10^5 g sPS/mol h.
[c] Determined by GPC.
[d] 10^4 g/mol.
[e] The percentage of sPS in the produced polystyrene.

when the polymerization was carried out at 90 °C over 4 h [8]. Under this condition, sPS obtained displayed a unimodal molecular weight distribution (entry 10, M_w/M_n 2.1) in a manner consistent with single-site catalysis.

Complexes **2a**–**e** showed similar catalytic behavior at 90 °C with Al/Ti ratio 3000 (entries 1–5, Table 4). The highest activity 1.8×10^5 g sPS/mol h was observed in the case of complex **2b** was applied, suggesting that the steric isopropyl does not influence the polymerization at 90 °C. The complexes activity was influenced by their electrophilic nature. Consequently, the activities increase in turn of **2c** = **2e** < **2a** < **2d**. The introduction of an electron-withdrawing CF_3^- group resulted in an improved catalytic activity of 1.7×10^5 g sPS/ mol h (entry 4). Introduction of a methyl group on enolate carbon induced a sharp loss of activity (entry 6). This is consistent with ethylene homopolymerization [4f]. Though we have tried to develop single crystals of **2f** to determine the structure difference, however many attempts failed. Zirconium complex **3** was also tried to catalyze the styrene polymerization. However, lower activity was observed under the same conditions. sPS was the only product when each of complexes **2a**–**e** was used, considering the formed aPS was always lower than that produced in the control experiment. However, in the case of **2f** and **3**, sPS percentage was 34% and 73% respectively even when the aPS produced in blank experiment was taken away from the product. The probable reason is that different active species formed in both of cases (entries 6, 7). GPC studies showed that the molecular weight varied in the range of tens of thousands, and the molecular weight distribution ranged from 2.0 to 3.3.

Conclusions

Titanium and zirconium complexes based on β-carbonylen-amine were prepared and fully characterized. In the presence of

MMAO, the titanium complexes showed high activity toward styrene polymerization with high syndiotacticity (up to 1.8×10^5 g sPS/mol h, sPS > 99%). The titanium showed good resistant toward high temperature, and the activity maintained even when the polymerization was carried out at 90 °C over 4 h. The zirconium complex could also polymerize styrene to syndiotactic polymers, but with low activity and low syndioselectivity.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.02.021.

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