Note

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

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A B S T R A C T

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]2ZrCl2(IV) could also polymerize styrene to give syndiotactic polymer, however in low activity and with low syndioselectivity.

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(phenoxylimine) complex and a hafnium pyridylamide complex [2b]. Fujita et al. revealed that bis(phenoxylimine) Ti complexes (Ti-FI catalysts) combined with dried MAO (DMAO) showed unique styrene polymerization behavior, and an IPS/PS 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 syndiacticity. 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. 1H NMR, 13C
NMR spectra were recorded on Varian Mercury 300 spectrometer and Varian 400 MR spectrometer. Mass spectra were obtained with a HP5899A spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). $M_n$, $M_w$, and $M_0/M_n$ 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 AXS8 X-ray diffractometer. Toluene, hexane, CH$_2$Cl$_2$ (DCM) and THF solutions were purified by MB SPS-800 system. Modified metalaluminoxane (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 [4e,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 2b (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$_3$): $\delta$ 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$_2$N), 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, CDCl$_3$): $\delta$ 189.4, 168.20(13), 162.3, 154.8, 145.0, 139.5, 135.2, 132.9, 128.9, 128.6, 127.3, 126.1, 104.6, 53.2, 34.6, 29.8. C$_{40}$H$_{44}$Cl$_3$N$_2$O$_2$S$_2$Zr (811.05): calcld 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, HCI/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 AXS8 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 differences 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

<table>
<thead>
<tr>
<th>Structure</th>
<th>Formula</th>
<th>$C_{15}H_{20}Cl_3NOSTi</th>
<th>C_{54}H_{58}N_2O_2S_2Zr</th>
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<td>Monoclinic</td>
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<tr>
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<td>14.419(6)</td>
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<tr>
<td>b, Å</td>
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<td>11.9417(5)</td>
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<tr>
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</tr>
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<td>γ, deg</td>
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<td>90</td>
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<tr>
<td>V, Å$^3$</td>
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<td>2376.07(17)</td>
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<td>Z</td>
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<td>2</td>
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<td>Full-matrix least-squares on $F^2$</td>
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<tr>
<td>wR2</td>
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<td>0.0602</td>
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### 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 C1–Ti–Cl2, Cl2–Ti–Cl3 and C1–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–Cl2, C13–S–Ti, and C12–S–Ti in complex 2c are 102.5(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.](image-url)
We tried to synthesize the zirconium analog under similar conditions (Scheme 2). However only bis[1,3-diphenyl-3-(2-isopropylthio)ethylimino]prop-1-en-1-olate Zr(IV) dichloride 3 could be separated after 1b was treated with ZrCl₄, no matter the 1b/ZrCl₄ molar ratio being 1/1 or 2/1.

The structure of 3 was determined by 1H NMR and 13C 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 1H NMR and 13C NMR signals of –CH₂N and –CH₂S move upfield obviously. For example, variations of 0.47 ppm and 1.5 ppm respectively in 1H NMR, and 4.2 and 7.6 ppm respectively in 13C 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 length of O₁–Zr–N₁ is 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); C₁–Zr–C₁₂, 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 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-butane (MEK) for 4 h to separate the polymer into two parts. The MEK-soluble polymer is atactic PS longingly the polymerization time had little influence on the activity (entries 6–12), and we found that the activity maintained even suggesting that the MEK-soluble portion produced in reaction system was mainly produced by MMAO. [3a,4b]

13C NMR spectroscopy of the 2-butane 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 × 10⁴ g sPS/mol h (entry 1, Table 2). The polymerization activity rose when further improving the polymerization temperature to 100 °C (6.0 × 10⁴ 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 × 10⁴ 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.](image)
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, Mw/Mn 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 × 10^4 g sPS/mol h was observed in the case of complex 2b, suggesting that the sterically hindered CF3 group resulted in an improved catalytic activity of 1.7 × 10^4 g sPS/mol h. Introduction of a methyl group on enolate carbon induced a sharp loss of activity (entry 6). This is consistent with ethylene homopolymerization [41]. Through these efforts, 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. 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-carbonyl enamine 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 × 10^4 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

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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.

References

