



Synthesis and structure of an air-stable bis(pentamethylcyclopentadienyl) zirconium pentafluorobenzenesulfonate and its application in catalytic epoxide ring-opening reactions

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ABSTRACT

An air-stable mononuclear complex of bis(pentamethylcyclopentadienyl) zirconium pentafluorobenzenesulfonate was successfully synthesized by treating $C_6F_5SO_3Ag$ with $[(CH_3)_5Cp]_2ZrCl_2$, which showed the cationic uninuclear structure of $[(CH_3)_5Cp]_2Zr(CH_3CN)_2(H_2O)[(OSO_2C_6F_5)_2 \cdot CH_3CN]$ (**1**) confirmed by the X-ray analysis. Complex **1** was also characterized by other techniques and found to have the good nature of air-stability, water tolerance, thermally-stability and strong Lewis-acidity. Moreover, the complex showed high catalytic activity and recyclability in catalytic epoxide ring-opening reactions by amines or alcohols. This catalytic system affords a simple and efficient approach for synthesis of β -amino alcohols or β -alkoxy alcohols.

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1. Introduction

Lewis acid promoted ring opening of epoxides with amines or alcohols is important organic transformation for production of β -amino alcohols or β -alkoxy alcohols, which are versatile intermediates in synthesizing a vast range of biologically active products, unnatural amino acids and chiral auxiliaries.¹ And ring-opening reaction of epoxides have been applied in the manufacture of drugs and pharmaceuticals,² such as (–)-swainsonine, HBV inhibitor and lasalocid (Fig. 1).

The classical protocol for synthesis of β -amino alcohols is direct aminolysis of epoxides at elevated temperatures in an excess amount of amines.³ Due to poor nucleophilicity of alcohols, alcoholysis of epoxides requires either strongly acidic or basic conditions.⁴ To avoid drawbacks of classical aminolysis protocol and

harsh conditions of alcoholysis, the various methods have been developed to open epoxide ring with amines or alcohols in the presence of Lewis acids catalysts such as $InCl_3$,⁵ $ZrCl_4$,⁶ $SbCl_3$,⁷ $ZnCl_2$,⁸ $BF_3 \cdot OEt_2$,⁹ Cp_2ZrCl_2 ,¹⁰ $Al(OTf)_3$,¹¹ $Cu(BF_4)_2$.¹² Nonetheless, there are disadvantages with those methods, e.g. using air-sensitive catalysts, elevated temperature, long reaction time, moderate yields, poor regioselectivity, high catalyst loadings and poor recyclability of catalysts. Thus, there is ongoing activity aimed to establish a more simple and efficient catalytic protocol to accomplish this transformation.

It is well known that zirconocene compounds have attracted much attention due to their broad application in organic synthesis.¹³ However, their potential as Lewis acid catalysts have rarely been reported, which may be resulted from the lower Lewis acidity of Cp_2ZrCl_2 and their derivatives.¹⁴ In 2006, Otera group found that the perfluorooctanesulfonate groups could be used as effective counter anions to increase the acidity as well as the water-tolerant ability.¹⁵ With this in mind, we have synthesized a series of air-stable zirconocene perfluoroalkyl(aryl)sulfonates complexes, which showed strong Lewis acidity and high catalytic activity in many organic reactions.¹⁶ It should be noted that the remarkable

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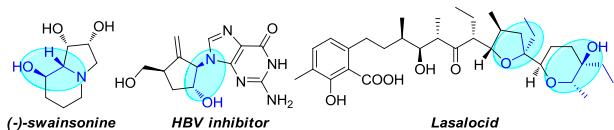


Fig. 1. Ring opening of epoxide applied in pharmaceuticals.

air-stability and strong Lewis acidity of these complexes mainly hinges on the perfluoroalkyl(aryl)sulfonate groups. However, their relatively low solubility in organic solvents owing to the strong lipophobic nature of perfluorooctanesulfonate group possibly declined the catalytic efficiency. To address this problem, we found that alkyl group incorporated with Cp ring can increase the solubility, as well as the catalytic efficiency.¹⁷ Also the lipophobicity of perfluorobenzenesulfonate group was weaker than that of the perfluorooctanesulfonate group, and the toxicity was lower than that of PFOS.¹⁸ Herein, we successfully synthesized and characterized bis(pentamethylcyclopentadienyl) zirconium pentafluorobenzenesulfonate $[[\{(\text{CH}_3)_5\text{Cp}\}_2\text{Zr}(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})][\text{OSO}_2\text{C}_6\text{F}_5]_2 \cdot \text{CH}_3\text{CN}$ (**1**). Moreover, we reported its catalytic application in epoxide ring-opening reactions by amines or alcohols in detail.

2. Results and discussion

Complex **1** was synthesized by treatment of $[(\text{CH}_3)_5\text{Cp}]_2\text{ZrCl}_2$ with $\text{AgOSO}_2\text{C}_6\text{F}_5$ (2 equiv) in CH_3CN solution, and the yield was 72% (Scheme 1).

The crystal structure of **1** in the solid state was confirmed by X-ray analysis. An ORTEP representation of **1** and selected bonds and angles were shown in Fig. 2. The crystal structure of complex **1** shows it is uninnuclear, which is different from the complex $[[\text{CpZr}(\text{OH}_2)_3]_2(\mu^2\text{-OH})_2][\text{SO}_3\text{C}_6\text{F}_5]_4 \cdot 6\text{H}_2\text{O}$, even though their synthetic procedures are identical.^{16b} In the crystal structure of **1**, the zirconium atom is stabilized by one water and two CH_3CN molecules, which also lie on the plane that bisects the angle between the Cp ring planes. The Zr-O and Zr-N distances of **1** are 2.242(5), 2.303(6) and 2.297(6) Å, respectively. The $\text{C}_6\text{F}_5\text{SO}_3^-$ ions and the dissociated CH_3CN molecule are packed around the complex cation and the C_6F_5 sides of the anion are clustered together to produce hydrophobic domains.

It is notable that the solid samples remained as dry crystals or powder after being kept in open air over three months. From the viewpoint of operation, such an excellent air-stable complex have great advantage over zirconocene bis(triflate) and the traditional Lewis-acid catalysts.¹⁹

The thermal behavior of complex **1** was investigated by TG-DSC under N_2 atmosphere (Fig. 3). The TG-DSC curves indicated three stages of weight loss. The endothermic step below 100 °C can be attributed to the removal of water and CH_3CN molecules. Complex **1** was stable up to about 260 °C. The weight loss of an exothermic nature at 300 °C is plausibly due to the oxidation of organic entities.

Conductivity measurement was applied to investigate its ionic dissociation behavior in CH_3CN (1.0mmolL^{-1}). The molar conductivity (Λ) of complex **1** thus measured at 20 °C was $137\ \mu\text{Scm}^{-1}$ (see

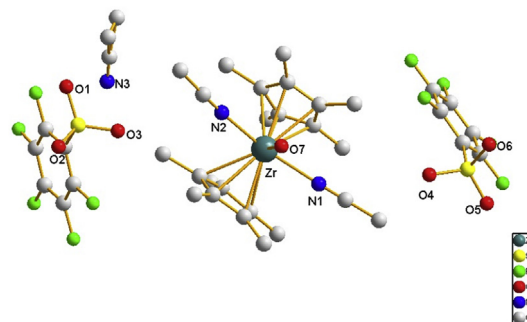


Fig. 2. The crystal structure of the complex **1** and selected bonds (Å) and angles (deg): The Zr1-O7, 2.242(5); Zr1-N1, 2.303(6); Zr1-N2, 2.297(6); Zr1-C18, 2.570(7); Zr1-C19, 2.552(7); Zr1-C20, 2.546(6); Zr1-C21, 2.526(7); Zr1-C22, 2.515(7); O7-Zr-N1 70.87(18); O7-Zr-N2 71.30(18); N2-Zr-N1 142.2(2); O7-Zr-C21 90.21(19).

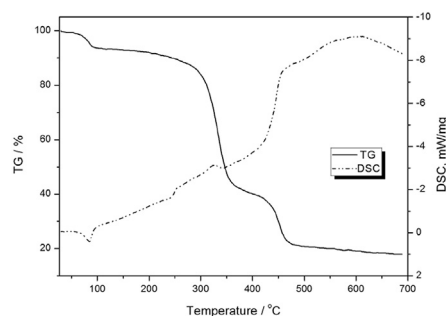


Fig. 3. TG-DSC curves of complex **1**.

Table S1 in ESI). The large molar conductivity value is consistent with the complete ionization into a 1:2 electrolyte,²⁰ implying that the complex is cationic in the solid as well as in the solution state. Another notable feature is the unusual solubility of **1** in Acetone, CH_3CN , THF, EtOAc and MeOH (Table 1). Actually, owing to the existence of ten methyl, one can see that complex **1** shows higher solubility in common polar organic solvents than the complex $[[\text{CpZr}(\text{OH}_2)_3]_2(\mu^2\text{-OH})_2][\text{SO}_3\text{C}_6\text{F}_5]_4 \cdot 6\text{H}_2\text{O}$.^{16b}

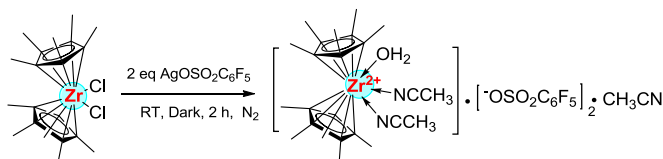
In addition, we estimated the Lewis acidity of complex **1** by the red shift (λ_{em}) of Lewis acid metal ions (Zr^{2+}) with 10-methylacridone on the basis of fluorescence spectra.²¹ The fluorescence maxima (λ_{em}) of complex **1** is 471 nm (see Fig. S1 in ESI). We also employed the Hammett indicator method to determine its acidity,²² and found that it showed a relatively strong acidity with the acid strength of $0.8 < H_0 < 3.3$ (H_0 being the Hammett acidity function; see Fig. S2 in ESI). These features facilitate its catalytic performance in catalytic epoxide ring-opening reactions.

In view of the strongly acidic character of complex **1**, 1.0 mol %

Table 1
The solubility of complex **1** in organic solvents at 25 °C.

Solvent	Solubility (g/L) of 1 ^a
Acetone	647
CH_3CN	842
THF	346
EtOAc	128
MeOH	384
Et_2O	16
CH_2Cl_2	0
<i>n</i> -Hexane	0
Toluene	0

^a The sample was freshly prepared and recrystallized in vacuum at room temperature in a period of 2 h.



Scheme 1. The synthetic route of complex **1**.

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