



Synthesis and structure of an air-stable μ^2 -hydroxy-bridged binuclear complex of bis(methylcyclopentadienyl)dizirconium(IV) perfluorooctanesulfonate and its application in Lewis acid-catalyzed reactions

Xiaohong Zhang^{a,b}, Cong Lou^b, Ningbo Li^a, Xinhua Xu^{a,*}, Renhua Qiu^a, Shuangfeng Yin^{a,*}

^a College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

^b College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China

ARTICLE INFO

Article history:

Received 18 August 2013

Received in revised form

29 September 2013

Accepted 1 October 2013

Keywords:

Bis(methylcyclopentadienyl)zirconium

perfluorooctanesulfonate

Lewis acid

Friedel–Crafts acylation

Mannich reaction

ABSTRACT

Air-stable binuclear complex of bis(methylcyclopentadienyl)zirconium perfluorooctanesulfonate (**1a**) was successfully synthesized by the reaction of $(\text{CH}_3\text{Cp})_2\text{ZrCl}_2$ with $\text{C}_8\text{F}_{17}\text{SO}_3\text{Ag}$. The compound **1a** was characterized by different techniques and found to have the nature of air-stability, water tolerance, thermally-stability and strong Lewis-acidity. In addition, its solubility was higher than that of our previously reported uninuclear zirconocene bis(perfluorooctanesulfonate). It showed high catalytic efficiency in the Friedel–Crafts acylation of alkyl aryl ethers and the Mannich reaction and could be reused.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Cationic zirconium compounds have aroused much interest in the past decades due to their comprehensive application in polymerization [1], ring-opening [2], cyclization [3], cycloaddition [4] or hydroamination reactions [5] and so on. Of the most interesting is bis(cyclopentadiene)zirconium dichloride [$(\text{Cp}_2\text{ZrCl}_2)$, Cp = cyclopentadiene] and its derivatives, which were widely applied in olefin polymerization and so on [1d,6]. However, Cp_2ZrCl_2 has rarely been used as Lewis acid in organic chemistry on account of its weak acidity [7]. Generally speaking, an organometallic Lewis acid should be as strongly acidic as possible to acquire higher activity. For example, Thewalt und Lasser [8] synthesized zirconocene triflates from the reaction of Cp_2ZrCl_2 with silver triflate, which was then employed by Bosnich [9] as an efficient Lewis acid catalyst to construct C–C bonds. Unfortunately, zirconocene triflates was found unstable in air owing to facile hydrolysis [9a]. In view of the practical application of cationic zirconocene derivatives as Lewis acid catalysts, it is highly deserved to lower the hygroscopic character while enhancing its Lewis acidity.

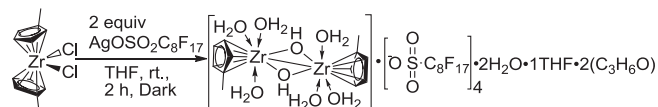
Recently, Otera and co-workers reported that the incorporation of perfluoroalkyl(aryl)sulfonate moieties to organometallic (ie., Sn, Zr, and Ti) cations could enhance acidity and stability [10]. With such understanding, several air-stable metallocene complexes bearing perfluorooctanesulfonate groups $(\text{Cp}_2\text{M}(\text{OSO}_2\text{C}_8\text{F}_{17}))_2$, M = Zr, Ti, Hf) were synthesized successively in our groups and were confirmed to show strong Lewis acidity and high catalytic activity in C–C bonds formation reactions [11]. However, their relatively low solubility in organic solvents owing to the strongly lipophobic nature of C_8F_{17} group maybe decline the catalytic efficiency. We envisioned that alkyl group incorporated with Cp ring will maybe increase the solubility as well as the catalytic efficiency. Based on this idea and in an attempt to expand the diversity of zirconocene catalysts, methyl was incorporated with the cyclopentadiene group to afford a novel and air-stable Lewis acidic organometallic species. Herein we report the synthesis and characterization of μ^2 -hydroxy bridged binuclear complex $[(\text{CH}_3\text{CpZr}(\text{OH})_2)_2(\mu^2\text{-OH})_2][\text{OSO}_2\text{C}_8\text{F}_{17}]_4 \cdot 2\text{H}_2\text{O} \cdot 1\text{THF} \cdot 2(\text{C}_3\text{H}_6\text{O})$ (denoted as **1a**·2H₂O·1THF·2(C₃H₆O) hereafter).

2. Results and discussion

The synthesis of **1a** was shown in Scheme 1. Treatment of bis(methylcyclopentadienyl)zirconium dichloride $[(\text{CH}_3\text{Cp})_2\text{ZrCl}_2]$ (1

* Corresponding authors. Fax: +86 731 88821546.

E-mail addresses: xhx1581@hnu.edu.cn (X. Xu), sf_yin@hnu.edu.cn (S. Yin).



Scheme 1. Synthesis of **1a**·2H₂O·1THF·2(C₃H₆O).

equiv) with silver perfluorooctanesulfonate (AgOSO₂C₈F₁₇) (2 equiv) in dry THF yielded **1a**·xH₂O·yTHF·z(C₃H₆O) (after recrystallization from THF-acetone). The water molecules in the complex originated from air or the solvent, and the hydrate numbers *x* and solvating ligands THF *y* varied according to the reaction conditions. The result of ¹H NMR spectroscopic (in dry [D₆] acetone) showed that in the freshly prepared sample after recrystallization and vacuum treatment at 60 °C for 1 h, the complex **1a**·xH₂O·yTHF became **1a** (*x* = 0, *y* = 0). It is notable that **1a**·xH₂O·yTHF suffered no color change over a month in air, suggesting that this complex can be considered to be air-stable and has a great advantage over zirconocene triflates in terms of operational point.

Though it is difficult to acquire the crystal structure owing to the large disorder of perfluorooctanesulfonate group, the cationic structure of **1a**·2H₂O·1THF·2(C₃H₆O) was fortunately confirmed by X-ray analysis after many trials. The crystals suitable for the X-ray diffraction were obtained by diffusion of hexane into saturated THF-acetone solution. The crystal structure and packing together with selected bonds and angles are shown in Fig. 1. Crystal data and structure refinement details are presented in Table 1. It can be seen

that bis(methyl) zirconocene in compound **1a** is cationic. It is very interesting to find that one of the MeCp ligands is removed and replaced by OH to form the binuclear structure, which is different from the uninuclear structure of Cp₂Zr(OSO₂C₈F₁₇)₂ [11d] even though their synthetic procedures are identical. The bridged Zr–O–Zr bonds of complex **1a** can stabilize the structure. And the zirconium atoms have a distorted octahedral coordination with the Cp group trans to the OH unit, similar to that of [(CpZr(OH)₂)₂(μ²-OH)₂]⁴⁺ [12]. The Zr(1)–O18, Zr(1)–O19, Zr(1)–O20, Zr(1)–O16, Zr(1)–O17 and Zr(2)–O21, Zr(2)–O22, Zr(2)–O23, Zr(2)–O16, Zr(2)–O17 distances of **1a**·2H₂O·1THF·2(C₃H₆O) are 2.186(5), 2.216(6), 2.167(5), 2.078(5), 2.166(5) and 2.158(5), 2.201(5), 2.185(6), 2.080(5), 2.154(5) Å, respectively. It can be found that the Zr–OH distances of **1a** are not similar to our previously reported Zr–OH complex [11b,12]. The different distances of Zr–O show that the OH group binds to the two Zr atoms unsymmetrically. The Zr(2)–O(16)–Zr(1) angle is 110.0(2) degree and the Zr–Zr distance is 3.4791(11), demonstrating that the Zr–Zr interaction is very weak. The C₈F₁₇SO₃[−] ions, the dissociated H₂O molecules, the solvating ligand THF and acetone are packed around the complex cation in such a way that their oxygen atoms point towards the H₂O ligands. The C₈F₁₇ chains of the anion, on the other hand, are clustered together to produce hydrophobic domains in the crystal structure.

The thermal behavior of complex **1a** was investigated by thermogravimetric-differential scanning calorimetry (TG–DSC) in nitrogen and air (Fig. 2). The TV–DSC curves indicate three stages of weight losses. The endothermic step below 100 °C can be attributed to the removal of water molecules. The material is stable up to

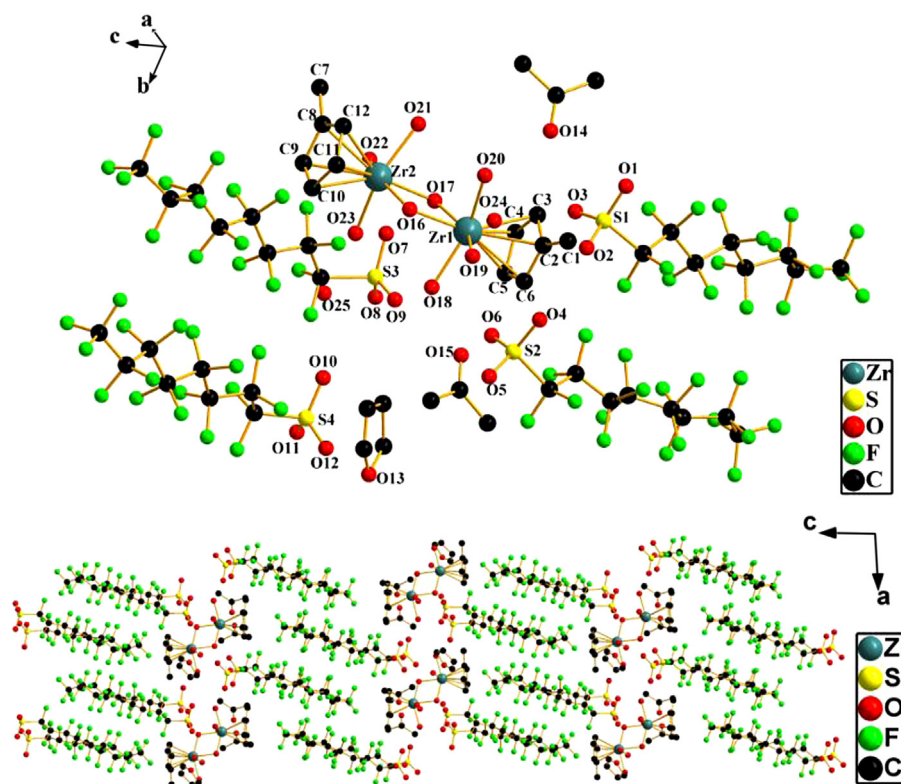


Fig. 1. Crystal structure and packing of [(CH₃CpZr(OH)₂)₂(μ²-OH)₂][OSO₂C₈F₁₇]₄·2H₂O·1THF·2(C₃H₆O) (**1a**·2H₂O·1THF·2(C₃H₆O)). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zr(1)–O18, 2.186(5); Zr(1)–O19, 2.216(6); Zr(1)–O20, 2.167(5); Zr(1)–O16, 2.078(5); Zr(1)–O17, 2.166(5); Zr(2)–O21, 2.158(5); Zr(2)–O22, 2.201(5); Zr(2)–O23, 2.185(6); Zr(2)–O16, 2.080(5); Zr(2)–O17, 2.154(5) Å; Zr(1)–C(5), 2.460(8); Zr(1)–C(4), 2.481(7); Zr(1)–C(3), 2.489(8); Zr(1)–C(6), 2.494(8); Zr(1)–C(2), 2.524(8); Zr(1)–Zr(2), 3.4791(11); O(17)–Zr(1)–O(16), 69.5(2); O(17)–Zr(1)–O(20), 94.8(2); O(16)–Zr(1)–O(20), 77.2(2); O(17)–Zr(1)–O(18), 94.5(2); O(16)–Zr(1)–O(18), 79.2(2); O(20)–Zr(1)–O(18), 149.7(2); O(17)–Zr(1)–O(19), 150.3(2); O(16)–Zr(1)–O(19), 80.9(2); O(20)–Zr(1)–O(19), 80.4(2); O(18)–Zr(1)–O(19), 77.4(2); O(17)–Zr(1)–C(5), 93.0(2); O(17)–Zr(1)–C(4), 77.0(2); C(5)–Zr(1)–C(4), 33.2(3); C(5)–Zr(1)–C(3), 54.9(3); C(4)–Zr(1)–C(2), 54.3(3); Zr(2)–O(16)–Zr(1), 110.0(2); Zr(1)–O(17)–Zr(2), 110.6(2). The planes of the two Cp rings are parallel.

Download English Version:

<https://daneshyari.com/en/article/1321359>

Download Persian Version:

<https://daneshyari.com/article/1321359>

[Daneshyari.com](https://daneshyari.com)