



Air-stable μ^2 -hydroxyl bridged cationic binuclear complexes of zirconocene perfluorooctanesulfonates: their structures, characterization and application

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ABSTRACT

Three air-stable zirconocene perfluoro-octanesulfonates were successfully synthesized by treatment of $C_8F_{17}SO_3Ag$ with $(RCp)_2ZrCl_2$ [R = H, *n*-Bu, *t*-Bu]. According to X-ray analysis, they have μ^2 -hydroxyl bridged cationic binuclear structures: (i) $[CpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2THF \cdot 4H_2O$ (**1a**·2THF·4H₂O), (ii) $[n-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 6H_2O$ (**2a**·6H₂O), and (iii) $[t-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2C_3H_6O \cdot 8H_2O$ (**3a**·2C₃H₆O·8H₂O). The ligands of water and organic molecules in the complexes originated from the moist air and solvent during their recrystallization. These complexes were characterized with different techniques, and found to show water tolerance, air/thermal stability as well as strong Lewis acidity. Moreover, the complexes showed highly catalytic activity in various reactions of C–C bond formation. With good recyclability, they should find wide applications in organic chemistry.

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1. Introduction

Cationic zirconium compounds have wide applications in organic chemistry¹ since the synthesis of Cp_2ZrCl_2 in 1961.² Among them, zirconocene derivatives were often used in olefin allylation and polymerization.³ Initially, researches were mainly focussed on the preparation of various zirconocene compounds such as $Cp_2Zr(OR)Cl$,⁴ $Cp_2Zr(keotone)Cl$,⁵ $Cp_2Zr(CO_2Me)-Cl$,⁶ $Cp_2ZrMe(THF)]^+[BPh_4]$,⁷ and $[Cp_2ZrR]^+$ cation.⁸ Subsequently, zirconocene complexes were developed to serve as efficient catalyst.⁹ For example, ansa-zirconocene ester enolates were used to catalyze the polymerization of methacrylates.¹⁰ Cationic zirconocene hydrides were also reported to possess highly catalytic ability.¹¹ The zirconocene-catalyzed asymmetric

methylalumination of terminal alkenes in the presence of water was developed by Wipf and Ribe.¹² Scott and coworkers investigated the synthesis of zirconium salicyloxazoline complexes and the catalytic mechanism for cyclohydro-amination reactions.¹³ Xi et al. reported the zirconocene-mediated intermolecular coupling of aromatic ketones and alkynes to give multiply substituted indene derivatives.¹⁴ Miller et al. found that diynes underwent coupling reaction with $Cp_2Zr(\eta^2-Me_3SiC)_2(py)$ to give dimeric macrocycles in moderate yields.¹⁵ It is obvious that zirconocene complexes have an important role in organometallic chemistry. However, their potential utilization as Lewis acid catalysts in organic reactions is rarely reported, plausibly due to the weak Lewis acidity of Cp_2ZrCl_2 and their derivatives.¹⁶

To address this problem, Thewalt and Lasser¹⁷ synthesized $Cp_2Zr(OTf)_2$ from the reaction of Cp_2ZrCl_2 with $AgOTf$ in 1983, which was later employed by Hollis's group as an efficient Lewis acid catalyst for the construction of C–C bonds.¹⁸ Unfortunately, the hygroscopic nature of $Cp_2Zr(OTf)_2$ limited its practical application.^{18a} Therefore, it is highly desirable to lower the hygroscopic nature while enhancing the Lewis acidity. In 2006, Otera

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and co-workers provided a novel organotin perfluorooctanesulfonates and found that the long perfluoroalkyl(aryl)sulfonate substituent could increase acidity and water-tolerant ability.¹⁹ With such understanding, several air-stable perfluorooctanesulfonate-bearing zirconocene complexes $[(RCp)_2Zr(OSO_2C_8F_{17})_2]$, R = H, Me, Et and *i*-Pr] were continuously synthesized in our group.²⁰ These complexes showed strong Lewis acidity and highly catalytic activity for C–C and C–O bond formation. Furthermore, with the existence of alkyl group, $(RCp)_2Zr(OSO_2C_8F_{17})_2$, R = Me, Et and *i*-Pr are more soluble in organic solvents and have higher activity than $Cp_2Zr(OSO_2C_8F_{17})_2$.

Recently, we found that one of the EtCp or MeCp ligands of $((RCp)_2Zr(OSO_2C_8F_{17})_2)$, R = Me, Et) can be substituted by OH to form stable binuclear structures, which are different from the uninuclear $((RCp)_2Zr(OSO_2C_8F_{17})_2)$, R = H, *i*-Pr) even though the synthetic procedures are identical.^{20c–e} Herein we put forth a full account of the synthesis and characterization of a series of air-stable μ^2 -hydroxyl bridged zirconocene perfluorooctane sulfonates: (i) $[CpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2THF \cdot 4H_2O$ (**1a**·2THF·4H₂O), (ii) $[n-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 6H_2O$ (**2a**·6H₂O), and (iii) $[t-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2C_3H_6O \cdot 8H_2O$ (**3a**·2C₃H₆O·8H₂O, C₃H₆O is acetone). We assessed their catalytic activities for the C–C bonds formation in Mannich reaction, the direct alkylation of 1,3-dicarbonyl derivatives, the Michael addition as well as aza-Friedel-Crafts and Friedel-Crafts acylation. These catalytic systems are highly efficient, eco-friendly and atom-economical in accord with the concept of green chemistry.

2. Results and discussion

Treatment of zirconium dichloride derivatives $[(RCp)_2ZrCl_2]$, for **1a**, R = H; for **2a**, R = *n*-Bu; for **3a**, R = *t*-Bu (1 equiv) with silver perfluoro-octanesulfonate ($AgOSO_2C_8F_{17}$) (2 equiv) in dry THF yields **1a**, **2a** and **3a**, respectively (Scheme 1). Though it is difficult to acquire the crystal structures owing to the large disorder of perfluorooctanesulfonate group, the structures of complexes **1a**, **2a** and **3a** were fortunately confirmed by X-ray analysis after many trials. The results showed that after recrystallization from THF (or acetone)-hexane, the samples **1a**, **2a** and **3a** have the following cationic structures: $[CpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2THF \cdot 4H_2O$ (**1a**·2THF·4H₂O), $[n-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 6H_2O$ (**2a**·6H₂O) and $[t-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2(C_3H_6O) \cdot 8H_2O$ (**3a**·2(C₃H₆O)·8H₂O). The crystal structures together with selected bonds and angles are shown in Figs. 1–3. The water and organic molecules in the complexes originated from the moist air and solvent during their

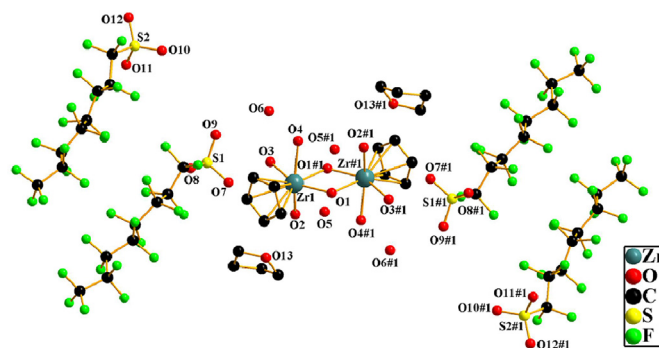
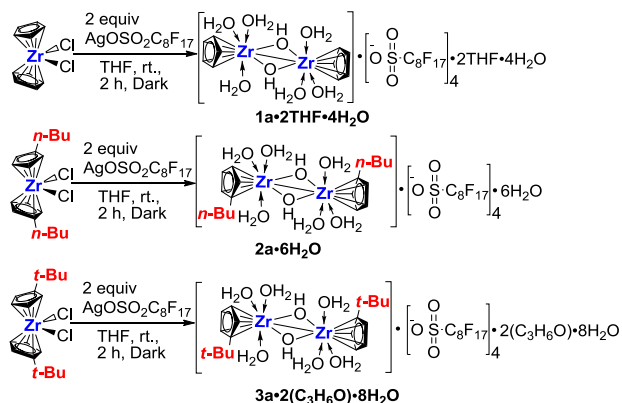


Fig. 1. Crystal structure of $[CpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2THF \cdot 4H_2O$ (**1a**·2THF·4H₂O). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zr(1)–O(1), 2.1026(17); Zr(1)–O(2), 2.1413(18); Zr(1)–O(#1), 2.1633(17); Zr(1)–O(4), 2.1994(18); Zr(1)–O(3), 2.2207(18); Zr(1)–C(5), 2.501(3); Zr(1)–C(1), 2.502(3); O(1)–Zr(1)–O(2), 96.72(7); O(1)–Zr(1)–O(#1), 69.24(7); O(1)–Zr(1)–C(5), 87.19(9); O(2)–Zr(1)–C(5), 127.63(8).

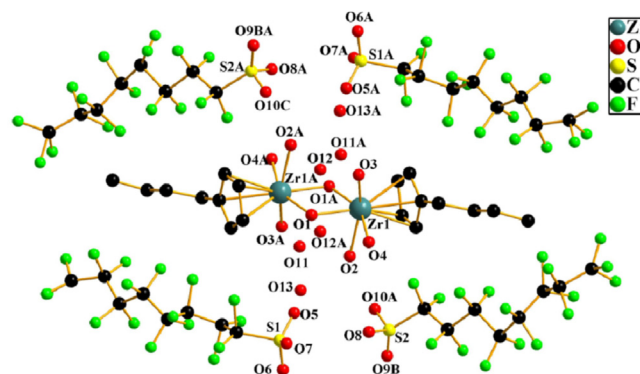


Fig. 2. Crystal structure of $[n-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 6H_2O$ (**2a**·6H₂O). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zr(1)–O(#1), 2.085(7); Zr(1)–O(3), 2.167(7); Zr(1)–O(1), 2.171(7); Zr(1)–O(2), 2.200(8); Zr(1)–O(4), 2.257(7); Zr(1)–C(2), 2.491(10); Zr(1)–C(1), 2.514(10); Zr(1)–C(4), 2.544(11); O(3)–Zr(1)–O(1), 79.2(3); O(#1)–Zr(1)–O(2), 91.8(3); O(1)–Zr(1)–C(1), 155.2(3); O(2)–Zr(1)–C(1), 79.4(3).

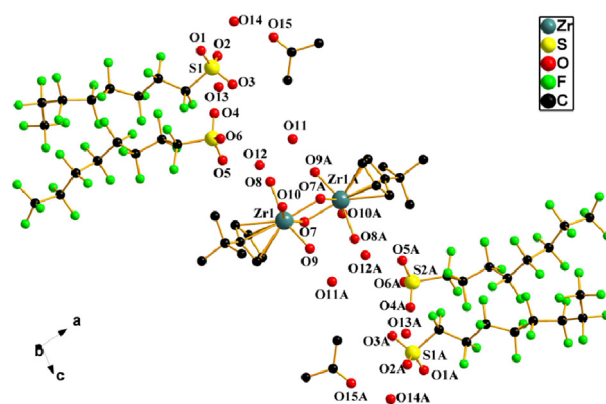


Fig. 3. Crystal structure of $[t-BuCpZr(OH_2)_3]_2(\mu^2-OH)_2(OSO_2C_8F_{17})_4 \cdot 2(C_3H_6O) \cdot 8H_2O$ (**3a**·2(C₃H₆O)·8H₂O). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zr(1)–O(7), 2.083(5); Zr(1)–O(8), 2.148(5); Zr(1)–O(9), 2.169(4); Zr(1)–O(#7), 2.175(4); Zr(1)–O(10), 2.224(5); Zr(1)–C(18), 2.456(6); Zr(1)–C(19), 2.466(6); O(7)–Zr(1)–O(8), 93.87(18); O(7)–Zr(1)–O(9), 93.46(18); O(8)–Zr(1)–C(19), 86.6(2); O(10)–Zr(1)–C(18), 130.5(2).

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