# Preparation of organozirconium aromatic compounds in mixed aqueous-organic solvents: X-ray structures of [Cp2ZrCl(μ2-O′,O″C-C6H5)], [(CpZr)3(μ2-O′,O″C-C6H3Cl2)3(μ3-OH)(μ2-OH)3](Cl2C6H3COO)2, and [(CpZr)3(μ2-O′,O″C-C6H4Cl)3(μ3-OH)(μ2-OH)3]Cl2·CH2Cl2

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## ARTICLE INFO

## ABSTRACT

A new and facile method is presented for the synthesis of zirconocene carboxylate compounds, in which zirconocene dichloride ($Cp_2ZrCl_2$) is dissolved in 1 M aqueous HCl solution and the requisite ligand is dissolved in an organic solvent. Five such compounds [$Cp_2ZrCl(\mu_2-O′,O″C-C_6H_5)$] (**1**), [$Cp_2ZrCl(\mu_2-O′,O″C-C_6H_3Cl_2)$] (**2**), [$Cp_2Zr(\mu_2-O′,O″C-C_6H_3(OH)Cl)_2$] (**3**), [$Cp_2Zr(\mu_2-O′,O″C-C_6H_3(OH)(NO_2))_2$] (**4**), and [$Cp_2Zr(\mu_2-O′,O″C-C_6H(OH)Cl_3)_2$] (**5**) have been obtained by this method. The effect of pH on the stability of $Cp_2ZrCl_2$ in 1 M HCl solution has been investigated by UV/vis spectrophotometry and ^{1}H NMR spectrometry. The results showed that the aqueous $Cp_2ZrCl_2$ solutions became less stable with increasing pH, liberating cyclopentadiene. Accordingly, at higher pH (∼7), two trinuclear zirconium monocyclopentadienyl compounds, [$(CpZr)_3(\mu_2-O′,O″C-C_6H_3Cl_2)_3(\mu_3-OH)(\mu_2-OH)_3$]($Cl_2C_6H_3COO)_2$ (**6**) and [$(CpZr)_3(\mu_2-O′,O″C-C_6H_4Cl)_3(\mu_3-OH)(\mu_2-OH)_3$]$Cl_2·CH_2Cl_2$ (**7**), were obtained. All compounds **1**–**7** have been characterized by FT-IR, ^{1}H NMR spectra and elemental analysis. In all of the compounds, the aromatic acid acts as a bidentate ligand in coordinating to the zirconium; both chelating and bridging modes are observed. X-ray crystallographic studies on **1**, **6**, and **7** have revealed that the geometries at zirconium are distorted octahedral in **6** and **7**, and distorted trigonal-bipyramidal in **1**.

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## 1. Introduction

Aqueous chemistry of organometallic compounds has attracted much attention owing to its potential to reduce organic solvent use and lower the associated impact on the environment [1–7]. In particular, zirconocene compounds, as highly active and selective polymerization catalyst precursors [8–23], and titanocene compounds, which show activity in the polymerization of styrene and methyl methacrylate in aqueous media [24,25], have received considerable interest in recent years. However, most organozirconocene compounds have hitherto been prepared under strictly anhydrous conditions. The complexity of aqueous systems containing zirconium can be attributed to the pronounced tendency of zirconium compounds to undergo hydrolysis reactions, even in strongly acidic solutions [26,27]. Recently, Butchard [28] reported the aqueous chemistry of the five-coordinate zirconocene dichloride [$PhP(CH_2CH_2-\eta^5-C_5H_4)_2ZrCl_2$] and summarized the work of a number of groups who have investigated the aqueous chemistry of zirconocene compounds.

Here, we present the pH dependence of the stability of zirconocene dichloride and the preparation of compounds **1**–**7**, extending our work on the aqueous chemistry of titanocene compounds. The stability of the zirconocene (Cp2Zr(IV) core) unit in 1 M aqueous HCl has been utilized in the synthesis of five benzoate derivatives of bis(cyclopentadienyl)zirconium(IV). Single-crystal X-ray analysis of **1** has shown it to be a typical bent-sandwich zirconocene benzoic acid compound. To the best of our knowledge, there has hitherto been few reports about zirconocene benzoate [29,30], and zirconocene salicylate compounds have not been reported until now. Reactions at higher pH, under which conditions the loss of cyclopentadiene is observed, lead to the formation of half-sandwich trinuclear zirconocene compounds **6** and **7**.

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## 2. Results and discussion

### 2.1. The pH dependence of the stability of $Cp_2ZrCl_2$ in aqueous solutions

Previously, we prepared and characterized substituted aromatic acid titanocene compounds in aqueous media [31–35]. Zirconocene compounds proved more problematic, probably due to the lability of $Cp_2ZrCl_2$ in aqueous solution. However, Baggio [36,37] succeeded in preparing the mononuclear eight-coordinate zirconium compound $[Zr\{(O(CH_2CO_2)_2)\}_2(H_2O)_2]\cdot4H_2O$ at pH 1.0–1.5 and the binuclear compound $K_6[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]\cdot4H_2O$ at pH 1.5. More recently, an interesting tetranuclear Zr(IV) species [3] was prepared in aqueous solution at pH 4. Though there were no cyclopentadienyl ligands in these compounds, these results suggest that aqueous organozirconium compounds can be prepared in acidic aqueous solutions. Thus, we studied the fate of $Cp_2ZrCl_2$ in aqueous solutions at different pH values, and found that it did not liberate cyclopentadienyl ligands in 1 M aqueous HCl at room temperature within 1 h, although higher pH did result in the release of cyclopentadiene.

Fig. 1 shows the UV spectrum of $Cp_2ZrCl_2$ (in $CH_2Cl_2$), along with the spectra of the materials **I** and **II** obtained upon dissolving $Cp_2ZrCl_2$ in dilute aqueous HCl at pH 1–2 (**I**) and in 1 M aqueous HCl (**II**).

The characteristic absorptions of both $Cp_2ZrCl_2$ and species **II** are seen at 233 nm and 290 nm, whereas species **I** only gives rise to the absorption at 233 nm in $CH_2Cl_2$ and a shoulder at 255 nm; no discernible absorption peak is observed at 290 nm. The similarity of the spectra of species **II** and $Cp_2ZrCl_2$ suggests that **II** may be $Cp_2ZrCl_2$ itself or a species that contains the bis(cyclopentadienyl)zirconium(IV) unit; the former assignment is supported by the ^{1}H NMR spectral results in Fig. 2.

The ^{1}H NMR spectrum of $Cp_2ZrCl_2$ in $D_2O$/HCl (1 M) shows only slight change with time. A new weak cyclopentadienyl resonance develops at $\delta = 6.12$ ppm after 30 min. More importantly, no free cyclopentadiene resonance is observed ($\delta = 2.9$ ppm) within 1 h. This gives a strong indication that $Cp_2ZrCl_2$ is comparatively stable in 1 M aqueous HCl solution for 30 min at ambient temperature, not undergoing irreversible hydrolysis with the release of free cyclopentadiene (Fig. 2).

The trace due to species **I** in Fig. 1 may be attributed to an irreversible hydrolysis product of $Cp_2ZrCl_2$, distinct from $Cp_2ZrCl_2$ itself, because of the conspicuous lack of an absorption at 290 nm. This suggests that $Cp_2ZrCl_2$ hydrolyzes irreversibly at pH 1–2. The ^{1}H NMR results in Fig. 3 confirm this notion.
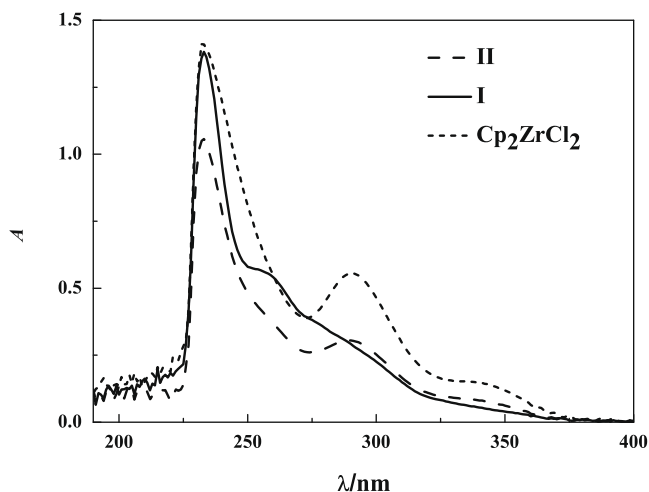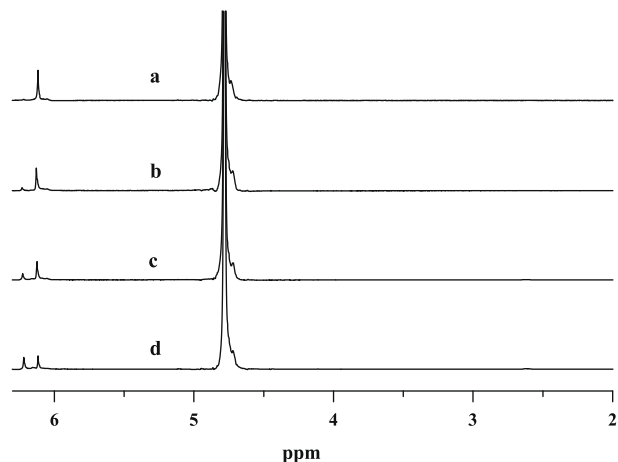


**Fig. 2.** ^{1}H NMR spectra of $Cp_2ZrCl_2$ in $D_2O$/HCl (1 M) after 0 min (a), 10 min (b), 0.5 h (c), and 1 h (d).
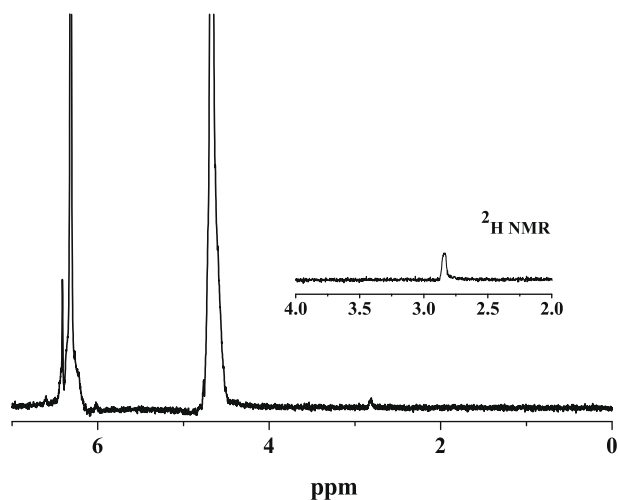


**Fig. 3.** ^{1}H NMR spectrum of $Cp_2ZrCl_2$ in $D_2O$/HCl (pH 1) after 5 min. Inset: the ^{2}H NMR spectrum, showing the appearance of a signal at $\delta = 2.9$ ppm (free $D^1$-cyclopentadiene) within 30 min.

The ^{1}H NMR spectrum of $Cp_2ZrCl_2$ in aqueous solution at pH 1 is shown in Fig. 3. A signal appeared at $\delta = 2.9$ ppm after 5 min, which intensified over the course of 30 min. A ^{2}H NMR analysis of the sample showed a signal at $\delta = 2.9$ ppm, the integral of which increased with time. Similar experiments at higher pH (up to pH 7.0) showed that the decomposition rate increased at higher pH. These results suggest that for the synthesis of bis(cyclopentadienyl)zirconium compounds in an aqueous system a low pH is required ($\sim$0) whereas higher pH values will result in Cp loss, giving mono(cyclopentadienyl)zirconium (or total Cp loss) zirconium units in the products.

### 2.2. Synthesis of $Cp_2ZrCl_n(O_2C\text{-}Ar)_{2-n}$ in mixed aqueous-organic solvent systems

Scheme 1 illustrates the synthetic protocol for the preparation of zirconocene compounds containing aromatic carboxylate ligands. In general, zirconocene dichloride (1 mmol) is dissolved in 1 M HCl and added to a solution of the aromatic acid in dichloromethane. Work-up affords compounds **1–5** in yields usually greater than 70%.
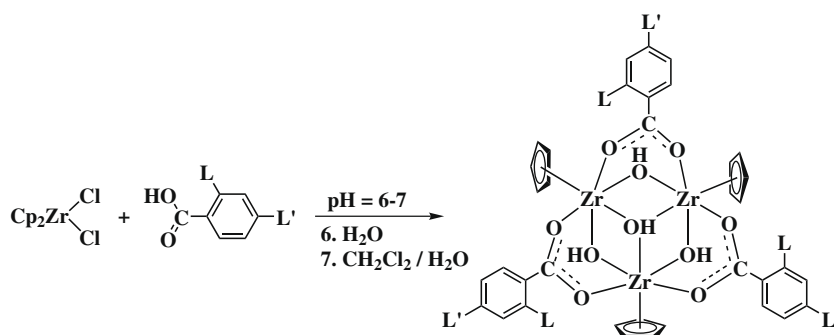
The analytical and NMR data for compounds **1–5** are consistent with the given formulations with appropriate chemical shifts and



**Fig. 1.** UV/vis spectra of **I**, **II**, and $Cp_2ZrCl_2$ in $CH_2Cl_2$.
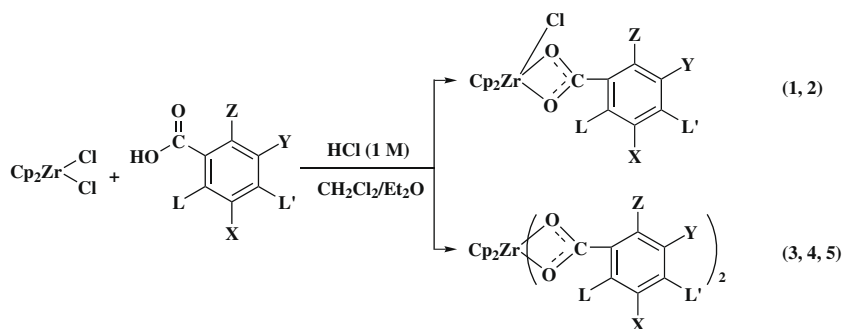
**1:** X=Y=Z=L=L'=H; **2:** X=Y=Z=H, L=L'=Cl; **3:** L=OH, X=L'=Z=H, Y=Cl;

**4:** L=OH, X=L'=Z=H, Y=NO$_2$; **5:** L=OH, X=Y=Z=Cl, L'=H;

**Scheme 1.**



**6:** L=L'=Cl; **7:** L=Cl, L'=H.

**Scheme 2.**

integrals in the NMR spectra. The IR spectra of compounds **1–5** show the characteristic peaks for Cp rings: strong bands located at 3092–3117 cm$^{-1}$ are assigned to the C–H stretching frequency; bands at 1424–1476 cm$^{-1}$ are attributed to C–C stretching vibrations; C–H in-plane deformation modes are observed at 1017–1021 cm$^{-1}$; and the C–H out-of-plane deformations are seen at 815–834 cm$^{-1}$ [38]. The bands appearing in the range 460–723 cm$^{-1}$ may be assigned to the various Zr–O bonds [38–40]. The asymmetric and symmetric stretching frequencies of the carboxylate groups help to assign the coordination of the oxygen atoms of these groups. In the spectra of compounds **1–5**, two strong bands are observed, which may be assigned to the $v_{asym}$(OCO) and $v_{sym}$(OCO) modes. The value of $\Delta(v_{asym} - v_{sym})$ has been used to determine the nature of the bonding of the carboxylate to metals; $\Delta(v_{asym} - v_{sym}) < 200$ cm$^{-1}$ is indicative of a bidentate carboxylate moiety and $\Delta(v_{asym} - v_{sym}) > 200$ cm$^{-1}$ is indicative of a monodentate carboxylate [29,41]. The $v_{asym}$(OCO) and $v_{sym}$(OCO) bands in the spectra of compounds **1–5** appear in the ranges 1618–1698 cm$^{-1}$ and 1481–1549 cm$^{-1}$, respectively, and the value of $\Delta(v_{asym} - v_{sym})$ is in the range 69–189 cm$^{-1}$, suggesting the presence of a bidentate coordination mode in these compounds. Indeed, the crystal structure of **1** (*vide infra*) shows bidentate coordination of the benzoate ligand. The structures of compounds **1** and **2** involve coordination by two Cp ligands, a chloride, and the two O atoms of the organic acid.

The broad bands seen at around 3430 cm$^{-1}$ in the spectra of compounds **3**, **4**, and **5** may be due to the O–H stretch of the hydroxy groups of the salicylate ligands. Compounds **3**, **4**, and **5** appear to be mononuclear, with the zirconium atom coordinated by two cyclopentadienyl ligands and two bidentate substituted salicylate anions. To further prove the structures of **1–5**, the silver nitrate solution was added to the dilute nitric acid solution of them, respectively, and the white precipitate were appeared for compounds **1** and **2**, while, **3–5**, still remained clarification, which confirmed that the Ti–Cl bond exist in compounds **1** and **2**. While in **3–5**, none Ti–Cl bonds were contained.

### 2.3. Synthesis of the half-zirconocene compounds **6** and **7** in an aqueous medium

In our previous work, when the reaction of titanocene and an organic acid was carried out at different pH values, using the same mixed-solvent method, two different titanocenes, mono- and bisubstituted with 5-nitrosalicylate, were obtained [33]. However, when we attempted to prepare zirconium compounds along similar routes (Scheme 2), using Cp$_2$ZrCl$_2$ in acetylacetone or dichloromethane solution, and reacting it with an aromatic ligand in aqueous solution at pH 7, different types of products were obtained, namely the *trinuclear* compounds **6** and **7**.

The analytical and spectral data of these two compounds are consistent with the given formulations and, in addition, the molecular structures of **6** and **7** were further determined by single-crystal X-ray diffraction analysis. The molecular structures of these compounds are quite different from those of the corresponding titanocene compounds [33,38]. It appears that the hydrolysis of the cyclopentadienyl ligands at pH ≈ 7 may be responsible for the product type as the same ligand is used in **2** and **6**; the pH of

**Table 1**
Crystal data and details of the structure refinement for compounds **1**, **6**, and **7**.

| Compound | **1** | **6** | **7** |
|---|---|---|---|
| | $C_{17}H_{15}ClO_2Zr$ | $C_{50}H_{34}Cl_{10}O_{14}Zr_3$ | $C_{37}H_{33}Cl_7O_{10}Zr_3$ |
| Formula weight | 377.96 | 1486.93 | 1159.04 |
| $T/K$ | 298(2) | 273(2) | 273(2) |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic |
| Space group | $Pnma$ | $P2_1/c$ | $P2_1/c$ |
| $a/Å$ | 13.09(3) | 18.430(4) | 17.249(5) |
| $b/Å$ | 10.76(2) | 20.380(4) | 18.130(5) |
| $c/Å$ | 11.18(2) | 14.731(3) | 14.385(4) |
| $\beta/(°)$ | 90 | 95.603(3) | 95.990(4) |
| $V/Å^3$ | 1573(6) | 5506(2) | 4474(2) |
| $Z$ | 4 | 4 | 4 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.596 | 1.794 | 1.721 l |
| $\mu$ (mm$^{-1}$) | 0.869 | 1.107 | 1.156 |
| $F(0\,0\,0)$ | 760 | 2944 | 2296 |
| Crystal dimensions (mm) | 0.43 × 0.27 × 0.22 | 0.46 × 0.41 × 0.19 | 0.47 × 0.16 × 0.14 |
| $2\theta$ range (°) | 2.40–25.11 | 1.49–25.03 | 1.63–25.07 |
| Limiting indices | −15 ⩽ h ⩽ 15 | −19 ⩽ h ⩽ 21 | −20 ⩽ h ⩽ 17 |
| | −12 ⩽ k ⩽ 10 | −17 ⩽ k ⩽ 24 | −21 ⩽ k ⩽ 18 |
| | −12 ⩽ l ⩽ 13 | −17 ⩽ l ⩽ 17 | −15 ⩽ l ⩽ 17 |
| Goodness-of-fit on $F^2$ | 1.12 | 1.021 | 1.003 |
| Total/unique/$R_{int}$ | 7726/1484/ 0.0489 | 28 334/9675/ 0.0537 | 22 913/7814/ 0.0314 |
| $R_1/wR_2$ | 0.0321/0.0816 | 0.0473/0.1217 | 0.0442/0.1255 |
| Peak and hole (e Å$^{-3}$) | 0.402/−0.811 | 0.976/−0.700 | 1.068/−0.711 |

the aqueous phase is the most prominent difference in the synthetic protocols.

## 2.4. Crystal structures of compounds 1, 6, and 7

Crystals of **1** suitable for X-ray diffraction analysis were obtained from a solution in dichloromethane/hexane at room temperature after storage for 2 weeks. Compound **1** was obtained as colourless block-like crystals, and proved to be remarkably stable when exposed to air. Crystal data and details of the structure refinement for **1** are presented in Table 1.

A perspective view of the structure of $[Cp_2ZrCl(\mu_2\text{-}O',O''\text{-}C_6H_5)]$ (**1**) showing the atom numbering scheme is presented in Fig. 4. Compound **1** crystallizes in the orthorhombic space group $Pnma$, as a mononuclear pentacoordinate compound consisting of one $Cp_2Zr$ fragment, one benzoate ligand, and one chloride ligand. Benzoic acid acts as a bidentate ligand and coordinates to the Zr to form a four-membered ring so that each Zr has two ligating oxygen atoms in addition to two Cp ligands and a chloride ligand, achieving an 18-electron configuration. The structure shows a typical
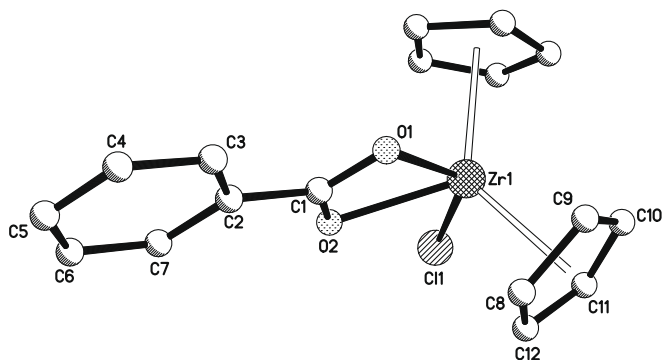
bent metallocene unit with pertinent bond angles O1–Zr1–O2 = 56.77(9)° and Cp–Zr1–Cp = 130.61(3)°, which are in good agreement with the corresponding angles in $[(\eta^5\text{-}C_5H_5)_2 ZrCl(OC_6H_4PPh_2)]$ (Cp1–Zr–Cp2 = 130.5(3)°) [42] and $[(\eta^5\text{-}C_5H_5)_2Zr(OC_6H_4PPh_2)_2]$ (Cp1–Zr–Cp2 = 127.7(5)°) [42]. The Zr–Cp lengths (2.227(4) Å) and Zr1–Cl1 (2.531(6) Å) are somewhat longer than those in $[(\eta^5\text{-}C_5H_5)_2ZrCl(OC_6H_4PPh_2)]$ [42]. The dihedral angle between the planar Cp fragments is 50.3(3)°. In addition, the two Zr–O bond lengths are slightly different (Zr1–O1 = 2.304(5) Å and Zr1–O2 = 2.260(3) Å). Selected bond lengths and angles are listed in Table 2.

Hydrogen bonds C5–H5···O1 ($x + 0.5$, $y$, $0.5 − z$) and C10–H10···O2 ($−x$, $y$, $1.5 − z$) exist in the crystal structure of **1**. Their bond lengths are 2.457 Å and 2.542 Å, and their bond angles are 179° and 153°, respectively. The adjacent molecules are linked by C5–H5···O1 to form a one-dimensional T-shaped chain. The supramolecular packing reveals that a two-dimensional network structure is further assembled by C10–H10···O2 hydrogen bonds. Furthermore, a three-centre (C–H)$_2$···O hydrogen bond is formed by two C–H···O intermolecular hydrogen bonds, in which atom O2 acts as an acceptor, and the two donors are C10, via atom H10, and C10*, via atom H10*. The combination of the three-centre (C–H)$_2$···O hydrogen bonds results in each molecule being closely associated with adjacent molecules to form a four-square lattice viewed along the $b$-axis, which propagates through C5–H5···O1 and C10–H10···O2 hydrogen bonds along the $a$ and $b$ axes, respectively, and assembles the lattices into a two-dimensional network structure (Fig. 5).

Single crystals of **6** and **7** were obtained by recrystallization from dichloromethane/hexane at room temperature for 1 month. Compound **6** was obtained in the form of colourless block-shaped crystals, while **7** was obtained as colourless diamond-like crystals. Both were found to be stable to $H_2O$ and $O_2$, with no reactions being observed on exposing them to moisture or air. Compounds **6** and **7** crystallize in the monoclinic space group $P2_1/c$; crystal data are given in Table 1. Compounds **6** $[(CpZr)_3(\mu_2\text{-}O',O''C\text{-}C_6H_3Cl_2)_3\text{-}(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3](Cl_2C_6H_3COO)_2$ and **7** $[(CpZr)_3(\mu_2\text{-}O',O''C\text{-}C_6H_4Cl)_3 (\mu_3\text{-}OH)(\mu_2\text{-}OH)_3]Cl_2\cdot CH_2Cl_2$ have similar molecular structures, as shown in Figs. 6 and 7, respectively.

X-ray structure analysis of compound **6** showed that the crystal contains a nearly equilateral triangular core of three Zr atoms. The Zr atoms are bridged by three 2,4-dichlorobenzoate ligands, together with a $\mu_3$-OH group, and are capped above and below by three $\mu_2$-OH groups. The spatial arrangement of three CpZr groups is propeller-like, with 2,4-dichlorobenzoate ligands in a $\mu_2\text{-}O',O''$ bridging mode; therefore, the molecule has approximate $C_3$ sym-



**Fig. 4.** The structure of $[Cp_2ZrCl(\mu_2\text{-}O',O''C\text{-}C_6H_5)]$ (**1**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms have been omitted for clarity.

**Table 2**
Selected bond lengths (Å) and bond angles (°) for **1**. (Cp: C8–C12: Cp(centroid)).

| *Bond distances (Å)* | | | |
|---|---|---|---|
| Zr1–Cp | 2.227(4) | Zr1–O1 | 2.304(3) |
| Zr1–Cl1 | 2.531(3) | Zr1–C8 | 2.524(3) |
| Zr1–O2 | 2.260(3) | Zr1–C10 | 2.514(3) |
| Zr1–C9 | 2.499(3) | Zr1–C12 | 2.517(4) |
| Zr1–Cl1 | 2.531(7) | O2–C1 | 1.267(6) |
| O1–C1 | 1.273(5) | | |
| *Bond angles (°)* | | | |
| Cp–Zr1–Cp | 130.61(3) | Cl1–Zr1–O2 | 135.04(7) |
| Cl1–Zr1–O1 | 78.24(6) | O1–Zr1–O2 | 56.77(9) |
| O1–Zr1–C8 | 72.79(9) | O1–Zr1–C9 | 79.20(13) |
| O1–Zr1–C10 | 111.04(12) | O1–Zr1–C11 | 124.21(9) |
| O1–Zr1–C12 | 99.906(11) | O2–Zr1–C8 | 89.97(10) |
| O2–Zr1–C9 | 118.54(15) | O2–Zr1–C10 | 141.24(9) |
| O2–Zr1–C11 | 120.54(11) | O2–Zr1–C12 | 91.99(9) |
| Zr1–O1–C1 | 92.1(2) | Zr1–O2–C1 | 93.7(2) |
| O1–C1–O2 | 117.5(3) | O1–C1–C2 | 121.2(3) |
| O2–C1–C2 | 121.3(3) | | |
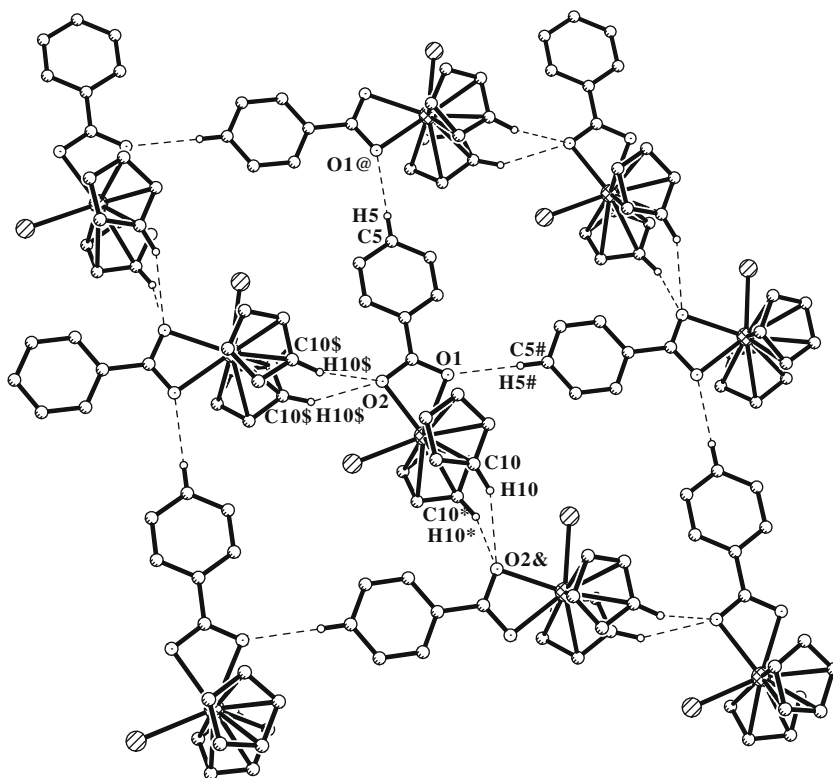
**Fig. 5.** The hydrogen-bond packing diagram of **1**. Symmetry codes: @ $(x + 0.5, y, 0.5 - z)$, $ $(x + 0.5, y, 1.5 - z)$, # $(-x, y, 0.5 - z)$, & $(-x, y, 1.5 - z)$.
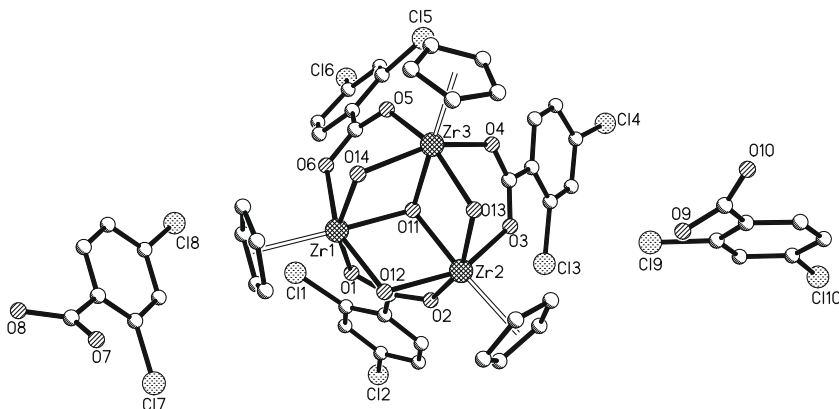


**Fig. 6.** The structure of $[(CpZr)_3(\mu_2-O',O''C-C_6H_3Cl_2)_3(\mu_3-OH)(\mu_2-OH)_3](Cl_2C_6H_3COO)_2$ (**6**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms have been omitted for clarity.

metry. The coordination sphere of six ligands about each zirconium atom is completed by the Cp ligand. The geometries at the zirconium atoms are distorted octahedral. The Zr–Zr distances in the nearly perfect triangle of zirconium atoms range from 3.3559(9) to 3.3594(10) Å, with an average of 3.3583 Å. These are comparable to those determined in $[(Cp^*Zr)_6(\mu_4-O)(\mu-O)_4(\mu-OH)_8]\cdot 2(C_7H_8)$ (3.564(1)–3.608(1) Å; average 3.586 Å) [2] and $[Zr_6(\mu_3-OH)_8(OH)_8(\kappa^2-bdmpza)_8]$ (3.497(2)–3.528(2) Å; average 3.509 Å) [43]. They are, however, significantly longer than those in $[\{(Et-Me_4C_5)Zr\}_6(\mu_6-O)(\mu_3-O)_8]\cdot(C_7H_8)$ (3.1542(9)–3.1709(11) Å; average 3.1635 Å) [2]. Selected bond lengths and angles of compound **6** are listed in Table 3.

The structure of compound **7** is similar to that of **6**, including the triangular core, with the Zr–Zr distances (Zr1–Zr2 = 3.3593(11) Å, Zr1–Zr3 = 3.3568(12) Å, Zr2–Zr3 = 3.3439(10) Å;

average 3.353 Å) being equal to within 0.0054 Å. Selected bond lengths and angles of **7** are listed in Table 4. In compound **7**, the three zirconium atoms and three $\mu_2$-OH oxygen atoms (O8, O9, and O10) give rise to a six-membered $Zr_3O_3$ ring with chair conformation. The bond lengths Zr–($\mu_2$-OH) (2.114(4)–2.138(4) Å; average 2.127 Å) and Zr–($\mu_3$-OH) (2.062(4)–2.085(4) Å; average 2.075 Å) (in compound **6**, the Zr–($\mu_2$-OH) bond lengths in the $Zr_3O_3$ ring range from 2.121(4) Å to 2.144(4) Å; average 2.135 Å) are similar to those in $[(Cp^*Zr)_6(\mu_4-O)(\mu-O)_4(\mu-OH)_8]\cdot 2(C_7H_8)$ (2.072(2)–2.171(2) Å; average 2.106 Å) [2] and $[(L_{OEt})_4Zr_4(\mu_3-O)_2(\mu-OH)_4(H_2O)_2][NO_3]_4$ (2.097(6)–2.157(7) Å; average 2.140(7) Å) [3], but a little shorter than those in $[(Cp_2Zr)_3(\mu_2-OH)_3(\mu_3-O)]BPh_4$ (2.186(3)–2.215(2) Å; average 2.196 Å) [44]. In **7**, the average O–Zr–O and Zr–O–Zr angles in the $Zr_3O_3$ ring are 92.11° and 104.06°, respectively (in compound **6**, they are
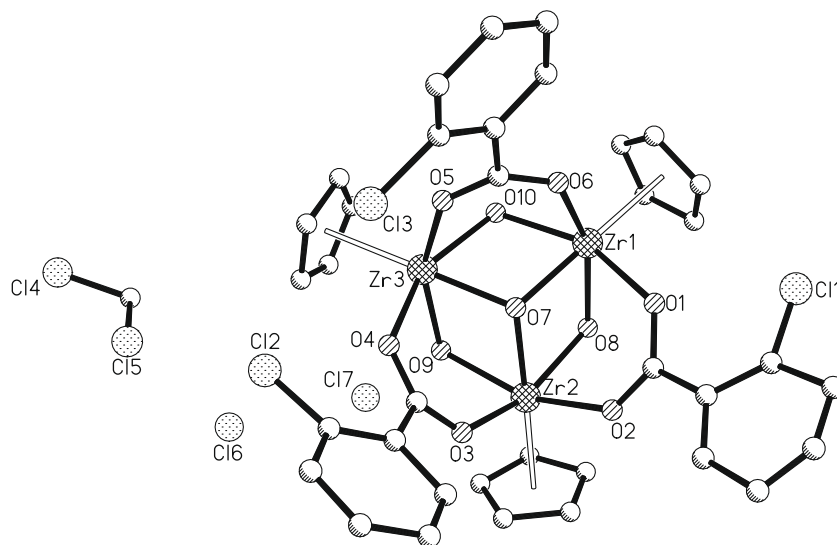
**Fig. 7.** The structure of [(CpZr)$_3$(μ$_2$-O′,O″C-C$_6$H$_4$Cl)$_3$(μ$_3$-OH)(μ$_2$-OH)$_3$]Cl$_2$·CH$_2$Cl$_2$ (**7**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms have been omitted for clarity.

**Table 3**
Selected bond lengths (Å) and angles (°) for compound **6**.

| Bond distances | | | |
|---|---|---|---|
| Zr1–Cp1 | 2.2399 | Zr1–O1 | 2.200(4) |
| Zr1–O6 | 2.187(4) | Zr1–O11 | 2.061(4) |
| Zr1–O12 | 2.144(4) | Zr1–O14 | 2.137(4) |
| Zr2–Cp2 | 2.2258 | Zr2–O2 | 2.196(4) |
| Zr2–O3 | 2.179(4) | Zr2–O11 | 2.072(4) |
| Zr2–O12 | 2.131(4) | Zr2–O13 | 2.133(4) |
| Zr3–Cp3 | 2.2249 | Zr3–O4 | 2.213(4) |
| Zr3–O5 | 2.182(4) | Zr3–O11 | 2.070(4) |
| Zr3–O13 | 2.121(4) | Zr3–O14 | 2.143(4) |
| Zr1–Zr2 | 3.3593(11) | Zr1–Zr3 | 3.3559(9) |
| Zr2–Zr3 | 3.3594(10) | | |
| *Bond angles* | | | |
| Cp1–Zr1–O1 | 101.27 | Cp1–Zr1–O6 | 99.82 |
| O1–Zr1–O6 | 85.42 | O11–Zr1–O12 | 73.36 |
| O11–Zr1–O14 | 73.04 | O12–Zr1–O14 | 93.09 |
| Cp2–Zr2–O2 | 103.62 | Cp2–Zr2–O3 | 100.02 |
| O2–Zr2–O3 | 84.38 | O11–Zr2–O12 | 73.42 |
| O11–Zr2–O13 | 72.68 | O12–Zr2–O13 | 94.95 |
| Cp3–Zr3–O4 | 102.42 | Cp3–Zr3–O5 | 102.05 |
| O4–Zr3–O5 | 82.47 | O11–Zr3–O13 | 72.97 |
| O11–Zr3–O14 | 72.75 | O13–Zr3–O14 | 90.65 |
| Zr1–O11–Zr2 | 108.75(16) | Zr1–O11–Zr3 | 108.68(13) |
| Zr2–O11–Zr3 | 108.42(17) | Zr1–O12–Zr2 | 103.62(16) |
| Zr2–O13–Zr3 | 104.34(17) | Zr1–O14–Zr3 | 103.28(16) |

Cp, the centroid of the C$_5$ ring: Cp1 (C36–C40), Cp2 (C41–C45), Cp3 (C46–C50).

**Table 4**
Selected bond lengths (Å) and angles (°) for compound **7**.

| Bond distances | | | |
|---|---|---|---|
| Zr1–Cp1 | 2.2536 | Zr1–O1 | 2.213(4) |
| Zr1–O6 | 2.212(4) | Zr1–O7 | 2.062(4) |
| Zr1–O8 | 2.126(4) | Zr1–O10 | 2.125(4) |
| Zr2–Cp2 | 2.2389 | Zr2–O2 | 2.203(5) |
| Zr2–O3 | 2.178(5) | Zr2–O7 | 2.085(4) |
| Zr2–O8 | 2.134(4) | Zr2–O9 | 2.125(4) |
| Zr3–Cp3 | 2.2473 | Zr3–O4 | 2.213(5) |
| Zr3–O5 | 2.175(4) | Zr3–O7 | 2.079(4) |
| Zr3–O9 | 2.114(4) | Zr3–O10 | 2.138(4) |
| Zr1–Zr2 | 3.3593(11) | Zr1–Zr3 | 3.3568(12) |
| Zr2–Zr3 | 3.3439(10) | | |
| *Bond angles* | | | |
| Cp1–Zr1–O1 | 100.80 | Cp1–Zr1–O6 | 101.52 |
| O1–Zr1–O6 | 85.41 | O8–Zr1–O7 | 73.53 |
| O7–Zr1–O10 | 73.53 | O8–Zr1–O10 | 92.07 |
| Cp2–Zr2–O2 | 101.43 | Cp2–Zr2–O3 | 100.99 |
| O2–Zr2–O3 | 84.82 | O7–Zr2–O8 | 72.92 |
| O7–Zr2–O9 | 73.56 | O8–Zr2–O9 | 92.28 |
| Cp3–Zr3–O4 | 101.84 | Cp3–Zr3–O5 | 101.2 |
| O4–Zr3–O5 | 85.03 | O7–Zr3–O9 | 73.9 |
| O7–Zr3–O10 | 72.92 | O9–Zr3–O10 | 91.98 |
| Zr1–O7–Zr2 | 108.19(17) | Zr1–O7–Zr3 | 108.29(17) |
| Zr2–O7–Zr3 | 106.82(17) | Zr1–O8–Zr2 | 104.11(17) |
| Zr2–O9–Zr3 | 104.15(17) | Zr1–O10–Zr3 | 103.91(16) |

Cp, the centroid of the C$_5$ ring: Cp1 (C22–C26), Cp2 (C27–C31), Cp3 (C32–C36).

92.90° and 103.75°, respectively), which are smaller than those in [(Cp$_2$ZrO)$_3$·C$_7$H$_8$] (average 97.47° and 142.50°, respectively) [45] and [(Cp$_2$Zr)$_3$(μ$_2$-OH)$_3$(μ$_3$-O)]BPh$_4$ (average 131.53° and 108.43°, respectively) [44]. The bond angles at the central oxygen atom in both compounds **6** and **7** are nearly the same (108°), as are the Zr–(μ$_3$-OH) bond lengths to the central oxygen atom (for **6**: Zr1–O11 = 2.061(4) Å, Zr2–O11 = 2.072(4) Å, Zr3–O11 = 2.070(4) Å; average 2.067 Å; for **7**: Zr1–O7 = 2.062(4) Å, Zr2–O7 = 2.085(4) Å, Zr3–O7 = 2.079(4) Å, average 2.075 Å). These bond lengths are similar to those in [(Cp$_2$Zr)$_3$(μ$_2$-OH)$_3$(μ$_3$-O)]BPh$_4$ (2.052(2)–2.070(4) Å; average 2.061 Å) [44], but shorter than those in [{(EtMe$_4$C$_5$)Zr}$_6$(μ$_6$-O)(μ$_3$-O)$_8$]·C$_7$H$_8$ (2.136(2)–2.169(2) Å; average 2.156 Å) [46] and [(η$^5$-C$_5$Me$_5$)ZrCl]$_3$(μ$_3$-O) (μ$_3$-OH)(μ$_2$-OH)$_3$· 2OC$_4$H$_8$ (2.198(4)–2.296(4) Å; average 2.277 Å) [47].

## 3. Conclusions

We have synthesized several organozirconium compounds in mixed aqueous/organic solvent systems. Organozirconocene compounds can be prepared by dissolving Cp$_2$ZrCl$_2$ in 1 M aqueous HCl solution (avoiding its hydrolysis) and then reacting it with the ligand dissolved in a polar organic solvent. At higher pH values, compounds containing a core of three mono(cyclopentadienyl)zirconium units complexed to aromatic carboxylates were obtained, presumably through an intermediate generated by the hydrolysis of a cyclopentadienyl ligand. These conditions are relatively straightforward in comparison to the traditional preparation of zirconocene complexes using Schlenk-line techniques.

## 4. Experimental

### 4.1. General remarks

^{1}H NMR spectra were obtained on a Bruker AVANCE 300 spectrometer and were calibrated using the solvent signals referenced to TMS. IR spectra were recorded in the range 4000–400 cm$^{-1}$ on a Perkin-Elmer FT-IR450 or Bruker EQUINOX 55 spectrometer with samples in KBr pellets. UV/vis spectra were recorded in the range 190–400 nm on a TU-1901 spectrophotometer from samples in dichloromethane solution in 1 cm quartz cells. Elemental analyses for C, H, and N were performed on a Perkin-Elmer Model 2400 analyzer. The single-crystal X-ray diffraction data were obtained on a Bruker Smart CCD 1000 diffractometer. All chemicals and reagents used were of analytical grade.

### 4.2. Stability of Cp$_2$ZrCl$_2$ in aqueous solution

Aliquots (1 mL) of concentrated aqueous HCl solution were added to respective solutions of Cp$_2$ZrCl$_2$ (0.2493 g, 1 mmol) in dilute aqueous HCl solution at pH 1–2 (10 mL) and in 1 M aqueous HCl (10 mL) at room temperature. The resulting mixtures were filtered, and the filtrates were extracted with dichloromethane. The organic layers were separated, dried with anhydrous MgSO$_4$, and filtered. The filtrates were concentrated in vacuo to give solids, designated as **I** and **II**, respectively.

Concentrated aqueous HCl solution (0.167 mL) was added to D$_2$O (1.833 mL) to yield 1 M D$_2$O/HCl. An aliquot (0.2 mL) of this solution was then diluted with further D$_2$O (1.8 mL) to provide 0.1 M (pH 1) D$_2$O/HCl. Other pH values were prepared accordingly. ^{1}H NMR spectra of the solutions were monitored over time.

### 4.3. Synthesis of [Cp$_2$ZrCl($\mu_2$-O',O''C-C$_6$H$_5$)] (**1**)

A mixture of Cp$_2$ZrCl$_2$ (0.2493 g, 1 mmol) in 1 M aqueous HCl solution (10 mL) and benzoic acid (0.1221 g, 1 mmol) in dichloromethane (15 mL) was stirred for 30 min at room temperature. The organic layer was separated, dried with anhydrous MgSO$_4$, and filtered. The filtrate was concentrated in vacuo to give a white solid (0.323 g, 85.4%), which proved to be extraordinarily stable in air. The compound was purified by recrystallization from CH$_2$Cl$_2$/hexane at room temperature. After 2 weeks, clear, colourless crystals suitable for single-crystal X-ray diffraction analysis had been deposited, with m.p. 151.9–152.5 °C. When silver nitrate solution was added to the dilute nitric acid solution of this colourless crystal, the white precipitate was appeared. Elemental analysis calcd. (%) for C$_{17}$H$_{15}$ClO$_2$Zr: C, 54.02; H, 4.00. Found: C, 53.97; H, 3.74%. ^{1}H NMR (CD$_3$COCD$_3$, 300 MHz): $\delta$ = 6.41 (s, 10H; C$_5$H$_5$), 7.52–8.05 (m, 5H; Ar). IR (KBr): $\nu$ = 3104, 1698, 1600, 1509, 1443, 1017, 873, 818, 728, 695, 460 cm$^{-1}$.

### 4.4. Synthesis of [Cp$_2$ZrCl($\mu_2$-O',O''C-C$_6$H$_3$Cl$_2$)] (**2**)

This compound was prepared in a similar manner to that described for **1**, starting from Cp$_2$ZrCl$_2$ (0.2493 g, 1 mmol) in 1 M aqueous HCl solution (10 mL) and 2,4-dichlorobenzoic acid (0.1910 g, 1 mmol) in CH$_2$Cl$_2$ (14 mL)/Et$_2$O (1 mL). The reaction afforded a colourless solid (0.343 g, 76.8%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O/hexane gave **2** as colourless crystals, with m.p. 149.4–150.8 °C. Like compound **1**, white precipitate was also appeared when silver nitrate solution was added to the dilute nitric acid solution of this colourless crystal. Elemental analysis calcd. (%) for C$_{17}$H$_{13}$Cl$_3$O$_2$Zr: C, 45.69; H, 2.93. Found: C, 45.62; H, 2.62%. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta$ = 6.35–6.50 (m, 10H; C$_5$H$_5$), 7.30–7.94 (m, 3H; Ar). IR (KBr): $\nu$ = 3092, 1645, 1587, 1518, 1481, 1424, 1371, 1019, 880, 816, 738, 567 cm$^{-1}$.

### 4.5. Synthesis of [Cp$_2$Zr($\mu_2$-O',O''C-C$_6$H$_3$(OH)Cl)$_2$] (**3**)

This compound was prepared in a similar manner to that described for **1**, starting from Cp$_2$ZrCl$_2$ (0.2493 g, 1 mmol) in 1 M aqueous HCl solution (10 mL) and 5-chloro-2-hydroxybenzoic acid (0.1726 g, 1 mmol) in CH$_2$Cl$_2$ (14 mL)/Et$_2$O (1 mL). The reaction afforded a pale-yellow solid (0.272 g, 96.3%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O/hexane gave **3**, with decomposition point 170.1–172.5 °C. When silver nitrate solution was added to the dilute nitric acid solution of **3**, the solution remained clarification. Elemental analysis calcd. (%) for C$_{24}$H$_{18}$Cl$_2$O$_6$Zr: C, 51.06; H, 3.21. Found: C, 50.87; H, 3.00%. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta$ = 6.36–6.42 (m, 10H; C$_5$H$_5$), 6.94–7.87 (m, 6H; Ar), 11.04 (s, 2H; –OH). IR (KBr): $\nu$ = 3434, 3243, 3114, 1626, 1582, 1532, 1470, 1409, 1385, 1355, 1244, 1020, 822, 723 cm$^{-1}$.

### 4.6. Synthesis of [Cp$_2$Zr($\mu_2$-O',O''C-C$_6$H$_3$(OH)(NO$_2$))$_2$] (**4**)

This compound was prepared in a similar manner to that described for **1**, starting from Cp$_2$ZrCl$_2$ (0.2493 g, 1 mmol) in 1 M aqueous HCl solution (10 mL) and 5-nitrosalicylic acid (0.1831 g, 1 mmol) in CH$_2$Cl$_2$ (15 mL)/Et$_2$O (3 mL). The reaction afforded a pale-yellow solid (0.206 g, 70.6%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O/hexane gave **4**, with decomposition point 233.4–235.5 °C. Like compound **3**, the solution remained clarification when silver nitrate solution was added to the dilute nitric acid solution of **4**. Elemental analysis calcd. (%) for C$_{24}$H$_{18}$N$_2$O$_{10}$Zr: C, 49.22; H, 3.10; N, 4.78. Found: C, 49.01; H, 2.71; N, 4.81%. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta$ = 6.22–6.65 (m, 10H; C$_5$H$_5$), 6.81–8.64 (m, 6H; Ar), 3.67 (s, 2H; –OH). IR (KBr): $\nu$ = 3425, 3108, 1673, 1630, 1593, 1543, 1518, 1476, 1434, 1339, 1301, 1020, 834, 712, 466 cm$^{-1}$.

### 4.7. Synthesis of [Cp$_2$Zr($\mu_2$-O',O''C-C$_6$H(OH)Cl$_3$)$_2$] (**5**)

This compound was prepared in a similar manner to that described for **1**, starting from Cp$_2$ZrCl$_2$ (0.2493 g, 1 mmol) in 1 M aqueous HCl solution (10 mL) and 2,3,5-trichloro-6-hydroxybenzoic acid (0.2415 g, 1 mmol) in CH$_2$Cl$_2$ (15 mL)/Et$_2$O (3 mL). The reaction afforded a pale-yellow solid (0.226 g, 64.4%). Recrystallization from CH$_2$Cl$_2$/hexane gave **5**, with decomposition point 209.2–210.7 °C. Like compound **3**, the solution remained clarification when silver nitrate solution was added to the dilute nitric acid solution of **5**. Elemental analysis calcd. (%) for C$_{24}$H$_{14}$Cl$_6$O$_6$Zr: C, 41.04; H, 2.01. Found: C, 40.95; H, 1.76%. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): $\delta$ = 6.16–6.57 (m, 10H; C$_5$H$_5$), 7.19–7.78 (m, 2H; Ar), 3.40 (s, 2H; –OH). IR (KBr): $\nu$ = 3423, 3117, 1618, 1549, 1440, 1396, 1358, 1225, 1021, 817, 565, 469 cm$^{-1}$.

### 4.8. Synthesis of [(CpZr)$_3$($\mu_2$-O',O''C-C$_6$H$_3$Cl$_2$)$_3$($\mu_3$-OH)($\mu_2$-OH)$_3$](Cl$_2$C$_6$H$_3$COO)$_2$ (**6**)

Cp$_2$ZrCl$_2$ (1.0 mmol) and acetylacetone (1.2 mmol) were dissolved in water (10 mL) and the mixture was stirred at ice-water temperature for 2 h to give a colourless solution. Meanwhile, 2,4-dichlorobenzoic acid (2 mmol) was dissolved in aqueous NaOH solution (20 mL) to give a sodium 2,4-dichlorobenzoate solution of pH 6.0–7.0. The Cp$_2$ZrCl$_2$ solution was then added to the benzoate solution over a period of 30 min with stirring at low temperature. After stirring at ice-water temperature for 4 h, the reaction mixture was filtered and the collected precipitate was washed with iced water, dried under vacuum overnight, and recrystallized from CH$_2$Cl$_2$/hexane. After about 1 month, colourless block-shaped crystals (1.141 g, 76.8%) suitable for single-crystal X-ray diffraction analysis were obtained, with m.p. 149.4–150.8 °C. Elemental analysis calcd. for C$_{50}$H$_{34}$Cl$_{10}$O$_{14}$Zr$_3$: C, 40.39; H, 2.30. Found: C, 40.62;

H, 2.12%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 6.35–6.50 (m, 15H; 3×C$_5$H$_5$), 7.30–7.94 (m, 15H; 5×ArH). IR (KBr): $\nu$ = 3432, 3092, 1645, 1587, 1518, 1481, 1424, 1371, 1019, 880, 816, 738, 567 cm$^{-1}$.

*4.9. Synthesis of [(CpZr)$_3$($\mu_2$-O',O''C-C$_6$H$_4$Cl)$_3$($\mu_3$-OH)($\mu_2$-OH)$_3$]Cl$_2$·CH$_2$Cl$_2$ (7)*

NaOH (1 mmol) and 2-chlorobenzoic acid (1 mmol) were dissolved in water (5 mL), and then hydrochloric acid was added until pH ≈ 6 was reached. This solution was added to a solution of Cp$_2$ZrCl$_2$ (1 mmol) in dichloromethane (15 mL) under vigorous stirring. The reaction mixture was stirred for 10 min at room temperature, and then the two-phase system was allowed to separate. The organic phase was dried over anhydrous MgSO$_4$, filtered, and the solvent was removed under reduced pressure. The residue was further dried under vacuum to give the crude product (0.723 g, 69.8%). M.p.: 255–257 °C. Elemental analysis calcd. for C$_{37}$H$_{33}$Cl$_7$O$_{10}$Zr$_3$: C, 38.33; H, 2.87. Found: C, 38.46; H, 2.78%. $^1$H NMR (300 MHz, [D$_6$]DMSO):$\delta$ = 6.44 (s, 15H; 3×C$_5$H$_5$), 7.10–8.74 (m, 9H; 3×ArH). IR (KBr): $\nu$ = 3421, 3102, 1641, 1585, 1518, 1481, 1424, 1331, 1018, 815, 744, 489 cm$^{-1}$.

*4.10. Crystal structure solution and refinement*

Diffraction data were collected at 298(2) K for **1** and 272(2) K for **6** and **7** on a Bruker Smart-1000 CCD detector, using graphite-monochromated Mo Kα radiation ($\omega−2\theta$ scans, $\lambda$ = 0.71073 Å). The structures were solved by direct methods and refined against $F^2$ by full-matrix least-squares techniques with Bruker's SHEXTL-97 program system [48]. All non-hydrogen atoms were refined using anisotropic thermal parameters by full-matrix least-squares calculations on $F^2$ using the program SHELXL-97 [49]. All hydrogen atoms were treated using a riding model. The crystals used for the diffraction studies showed no decomposition during data collection.

## Acknowledgments

## Appendix A. Supplementary data

CCDC 228494, 242064 and 242065 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.032.

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