

Crystal Structure of Chlorocyclopentadienylbis(1,3-diphenyl-1,3-propanedionato)zirconium(IV) Complex

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The group IV compound containing ligands such as a π -cyclopentadienyl, a chloride, and a bidentate β -diketonate presents an interesting opportunity to examine the properties of the three classes of ligands. The preparation of the CpM(IV)Cl(β -diketonato)₂ complex has been reported from Cp₂MCl₂ (M = Ti, Zr) with β -diketone (β -diketone = 2,4-pentanedione, 1-phenyl-butane-1,3-dione, 1,3-diphenyl-1,3-propanedione) with or without triethylamine.^{1,2} Recently we have reported the synthesis and structural properties of Cp₂(1-phenyl-1,3-butanedionato)Ti(III)³ and Cp₂(1,3-diphenyl-1,3-propanedionato)Ti(III)³ from the reaction mixture of “Cp₂Ti”^{4,5} which is prepared from Cp₂TiCl₂ and 2 equiv of *n*-BuLi with β -diketone such as 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione, along with catalytic studies for the mixture of Cp₂(1-phenyl-1,3-butanedionato)Ti(III) and Cp₂(1,3-diphenyl-1,3-propanedionato)Ti(III) and MMAO toward polymerization of ethylene.⁶ *cis*-CpZr(acac)₂Cl was formed from the reaction mixture of “Cp₂Zr”^{4,5} prepared from Cp₂ZrCl₂ and 2 equiv of *n*-BuLi with 2,4-pentanedione.⁷ Extension of the above reaction to a half-metallocenetitaniumtrichloride complex such as CpTiCl₃ or Cp*TiCl₃ resulted in the formation of CpTi(IV)(β -diketonato)Cl₂ (β -diketonato = 2,4-pentanedionato, 2,2,6,6-tetramethyl-3,5-heptanedionato)⁸ or Cp*Ti(IV)(β -diketonato)Cl₂ (β -diketonato = 2,4-pentanedionato and 1,3-diphenyl-1,3-propanedionato),⁹ when the appropriate β -diketone was allowed to react with the mixture from CpTiCl₃ or Cp*TiCl₃ and *n*-BuLi, respectively. We report the alternative preparation of Cp(acac)₂ZrCl₂ (**1**) and CpZr(1,3-diphenyl-1,3-propanedionato)₂Cl (**2**) and the structural characterization of **2** (Scheme 1).

Experimental Section

Materials. CpZrCl₃, *n*-butyllithium, and 1,3-diphenyl-1,3-propanedione were purchased from Aldrich and used without further purification. THF(tetrahydrofuran), ether, and dichloromethane were distilled from sodium, from potassium/benzophenone ketyl, and from P₂O₅ under nitrogen, respectively.

Measurements. Infrared spectra were recorded on a Shimadzu FTIR-8300. ¹H NMR (300 MHz) and ¹³C-NMR (75.5 MHz)spectra were recorded on a Bruker instrument at

room temperature and chemical shift in CD₂Cl₂ were given in ppm relative to tetramethylsilane as internal reference.

X-ray Single Crystal Structure Determination. The data for X-ray structure determination was collected on a CAD-4 diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. The unit cell dimensions were determined on the basis of 23 reflections in the range of $11.42^\circ < \theta < 13.88^\circ$. The data was collected by the $\omega/2\theta$ scan mode. The standard direct method was used to position the heavy atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms ($B_{iso} = 1.2B_{eq}$). The structure was refined in a full matrix least-squares calculation on F^2 . Program used to solve structure and to refine structure; SHELXS97 and SHELXL97.¹⁰ Molecular graphics; Ortep-3 for windows.¹¹

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-262132). The data can be obtained free of charge via www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Synthesis.

Chlorocyclopentadienybis(2,4-pentanedionato)zirconium(IV) (1): To a stirred solution of CpZrCl₃ (0.10 g, 0.38 mmol) in 30 mL of toluene was added *n*-butyllithium (0.31 mL, 0.78 mmol, 2.5M in hexane) under argon at -78°C . The mixture was stirred for 20 min, and 2,4-pentanedione (78 μL , 0.76 mmol) was added. The mixture was stirred for 24 h at RT, after which a resulting transparent solution was reduced in volume under reduced pressure to remove volatile materials. The residue was taken up in dichloromethane (20 mL) and filtered through Celite, and the filtrate reduced in volume to 10 mL. Crystallization by slow diffusion of hexane into the dichloromethane solution gave **1** as off-white cubes (0.12 g, 0.31 mmol, 81%).

Chlorocyclopentadienybis(1,3-diphenyl-1,3-propanedionato)zirconium(IV) (2): To a stirred solution of CpZrCl₃ (0.202 g, 0.77 mmol) in 30 mL of toluene was added *n*-

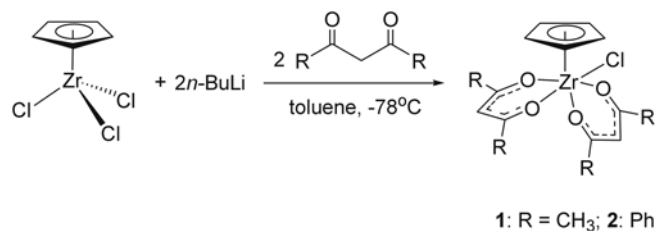
butyllithium (0.62 mL, 1.55 mmol, 2.5M in hexane) under argon at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred for 20 min, and 1,3-diphenyl-1,3-propanedione (0.347 g, 0.155 mmol, 10 mL toluene) was added. The mixture was stirred for 24h at RT, after which a resulting yellow solution was reduced in volume under reduced pressure to remove volatile materials. The residue was taken up in dichloromethane (20 mL) and filtered through Celite, and the filtrate reduced in volume to 10 mL. Crystallization by slow diffusion of ether into the dichloromethane solution gave **2** as yellow cubes (0.290 g, 0.45 mmol, 59%). IR (Nujol cm^{-1}) 3090 (w), 1597 (vs), 1556 (vs), 1516 (br vs), 1477 (vs), 1450 (s), 1441 (s), 1356 (s), 1325 (s), 1302 (s), 1227 (s), 1182 (m), 1159 (vw), 1126 (vw), 1096 (m), 1072 (m), 1020 (m), 999 (w), 972 (vw), 943 (m), 912 (vw), 846 (vw), 814 (s), 789 (m), 766 (s), 721 (vs), 689 (s), 617 (m), 534 (m). ^1H NMR (CD_2Cl_2) δ 8.17-7.02 (c, 20H, phenyl protons), δ 7.03 (s, 1H, CH), δ 7.02 (s, 1H, CH), δ 6.72 (s, 5H, C_5H_5). ^{13}C NMR (CD_2Cl_2) δ 185.2, δ 184.0, δ 183.9, δ 180.3 (s, CO), δ 137.5, δ 137.40, δ 132.8, δ 132.7, δ 132.6, δ 132.5, δ 129.0, δ 129.0, δ 128.8, δ 128.6, δ 128.2, δ 128.2, δ 128.1, δ 127.8 (all phenyl carbons), δ 117.6 (C_5H_5), δ 96.9 (CH), δ 96.0 (CH).

Results and Discussion

The reaction of 2 equiv. of diketone such as 2,4-pentanedione and 1,3-diphenyl-1,3-propanedione with the mixture generated from CpZrCl_3 and 2 equiv of *n*-BuLi in toluene at $-78\text{ }^{\circ}\text{C}$ resulted in the formation of $\text{Cp}(\text{acac})_2\text{-ZrCl}_2$ (**1**) and $\text{CpZr}(\text{1,3-diphenyl-1,3-propanedionato})_2\text{Cl}$ (**2**) (Scheme 1), respectively.

Complexes **1** and **2** have been prepared,^{1a,12} however, X-ray crystal structure for **2** has not been known so far. Thus we have performed X-ray crystal determination to garner more structural information about **2**. The data collection and structure solution parameters for **1** are given in Table 1. The molecular geometry and probability ellipsoids along with the numbering schemes are given Figure 1, and selected bond lengths and angles are listed in Table 2.

The molecular structure of complex **2** can be described as the *cis* configuration on an distorted octahedron which has a plane containing three oxygen atoms (O1, O6 and O10) and one chlorine atom as shown on Figure 1. The two remaining octahedral sites are occupied by the cyclopentadienyl ligand and the remaining oxygen atom (O5). The average Zr-O distance of 2.1324 Å is in good agreement with those reported for $\text{CpZr}(\text{acac})_2\text{Cl}$ (2.142(2) Å)⁷ and for the



Scheme 1. Synthesis pathway of the complexes **1** and **2**.

Table 1. Crystallographic data of complex **1**

Empirical formula	TiC ₁₅ H ₂₂ Cl ₂ O ₂
FW (amu)	353.13
Crystal system	Monoclinic
Space group	P 21/c
Radiation (Mo K α) ($\lambda/\text{\AA}$)	0.71073
a (\AA)	8.5142(17)
b (\AA)	26.235(5)
c (\AA)	8.4029(17)
α ($^{\circ}$)	90
β ($^{\circ}$)	116.16(3)
γ ($^{\circ}$)	90
V (\AA^3)	1684.7(6)
Z	4
$d_{\text{calcd.}}$ (Mg m^{-3})	1.392
Absorption coefficient, μ (mm^{-1})	0.823
F (0 0 0)	736
θ range for data collection ($^{\circ}$)	2.67 to 27.47
Reflection collected / unique	4095 / 3852 [R(int) = 0.0564]
Data / restraints / parameters	3852 / 0 / 166
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0885, wR_2 = 0.2003
Largest diff. peak and hole ($\text{e}\text{\AA}^{-3}$)	0.654 and -0.662

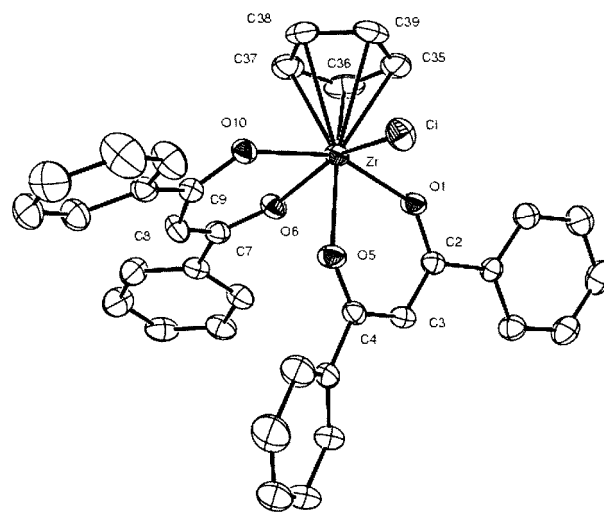


Figure 1. ORTEP drawing of the complex **2**, showing the atom numbering scheme and 30% probability ellipsoids. H atoms have been omitted for clarity.

Table 2. Selected bond lengths (\AA) and angles (deg) for complex **2**

Zr-O(1)	2.1065(19)	Zr-C(35)	2.523(3)
Zr-O(5)	2.1703(19)	Zr-C(36)	2.508(3)
Zr-O(6)	2.1532(19)	Zr-C(37)	2.538(3)
Zr-O(10)	2.0994(18)	Zr-C(38)	2.555(3)
Zr-Cl	2.4872(9)	Zr-C(39)	2.552(3)
O(10)-Zr-O(1)	153.51(7)	O(6)-Zr-O(5)	76.16(8)
O(10)-Zr-O(6)	78.94(7)	O(10)-Zr-Cl	88.44(6)
O(1)-Zr-O(6)	86.01(8)	O(1)-Zr-Cl	96.57(6)
O(10)-Zr-O(5)	78.06(7)	O(6)-Zr-Cl	154.91(6)
O(1)-Zr-O(5)	77.23(7)	O(5)-Zr-Cl	80.08(6)

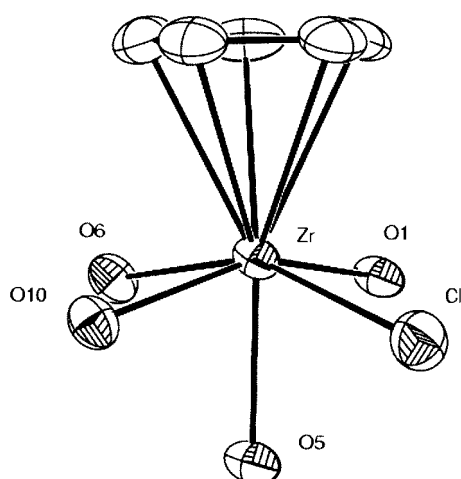


Figure 2. Distorted octahedral geometry around Zr metal.

Zr(acac)₄ (2.198(9) Å),¹³ and for the Zr(C₂O₄)₄⁴⁻ (2.199(9) Å).¹³ The Zr-Cl distance of 2.4872(9) Å in **2** is also similar to that found for CpZr(acac)₂Cl (2.5046(11) Å).⁷ The bond angles of O1-Zr-O5 (77.23(7)°) and O6-Zr-O10 (78.94(7)°) are comparable to those reported for CpZr(acac)₂Cl (79.48(9)° and 77.94(10)°).⁷ The reactions of β-diketones with the reaction mixture of CpHfCl₃ and *n*-BuLi have been undertaken. They gave different kinds of β-diketonate complexes, which will be reported separately.

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