

## Syntheses and Crystal Structure of Cp\*Ti( $\beta$ -diketonato)Cl<sub>2</sub> Complexes

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Received July 20, 2005

**Key Words :** Titanium(IV) complex,  $\beta$ -Diketonate, Pentamethylcyclopentadienyl, Crystal structure

The synthesis of  $\beta$ -diketonate complexes of an early transition metal has been extensively studied and generally involves the reaction of Cp<sub>2</sub>TiCl<sub>2</sub> with  $\beta$ -diketones in the presence of amine, or with the sodium salt of a  $\beta$ -diketone or protonolysis of Cp\*TiMe<sub>3</sub> with  $\beta$ -diketone.<sup>1,2</sup> Recently, we have investigated the reactivity of "Cp<sub>2</sub>M" (M=Ti, Zr)<sup>3,4</sup> prepared from Cp<sub>2</sub>MCl<sub>2</sub> and *n*-BuLi toward  $\beta$ -diketone, and reported several papers related to the syntheses and structural characterization of  $\beta$ -diketonate titanium complexes such as (acac)<sub>3</sub>Ti(III),<sup>5</sup> (1,3-diphenyl-1,3-propanedionato)<sub>3</sub>Ti(III),<sup>6</sup> Cp<sub>2</sub>(1-phenyl-1,3-butanedionato)Ti(III), Cp<sub>2</sub>(1,3-diphenyl-1,3-propanedionato)Ti(III),<sup>7</sup> and *cis*-CpZr(acac)<sub>2</sub>Cl.<sup>8</sup> Catalytic studies of Cp<sub>2</sub>(1-phenyl-1,3-butanedionato)Ti(III) and Cp<sub>2</sub>(1,3-diphenyl-1,3-propanedionato)Ti(III) toward polymerization of ethylene have also been studied.<sup>9</sup> Extension of the above reaction to the half-sandwich complexes such as CpMCl<sub>3</sub>, M=Ti and Zr, resulted in the formation of CpTi( $\beta$ -diketonato)Cl<sub>2</sub> or CpZr( $\beta$ -diketonato)<sub>2</sub>Cl ( $\beta$ -diketonato = acac, 2,2,6,6-tetramethyl-3,5-heptanedionato, and 1,3-diphenyl-1,3-propanedionato),<sup>10,11</sup> when the appropriate  $\beta$ -diketone was allowed to react with the mixture from CpMCl<sub>3</sub> and *n*-BuLi. We report here the preparation and the structural characterization of half-sandwich dichloro  $\beta$ -diketonate titanium complexes, Cp\*Ti( $\beta$ -diketonato)Cl<sub>2</sub> (Cp\* = pentamethylcyclopentadienyl,  $\beta$ -diketonato = acac (1), 1,3-diphenyl-1,3-propanedionato (2)).

### Experimental Section

**Materials.** Cp\*TiCl<sub>3</sub>, *n*-butyllithium, 2,4-pentanedione, and dibenzoylmethane were purchased from Aldrich and used without further purification. Hexanes and dichloromethane were distilled from potassium/benzophenone ketyl and from P<sub>2</sub>O<sub>5</sub> under nitrogen, respectively.

**Measurements.** Infrared spectra were recorded on a Shimadzu FTIR-8300. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C-NMR (75.5 MHz) spectra were recorded on a Bruker instrument at room temperature and chemical shift in CD<sub>2</sub>Cl<sub>2</sub> were given in ppm relative to tetramethylsilane as an 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 $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293 K. The unit

cell dimensions were determined on the basis of 23 reflections in the range of 11.35° <  $\theta$  < 12.64°. 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*<sub>iso</sub> = 1.2 *B*<sub>eq</sub> and 1.5 *B*<sub>eq</sub>). The structure was refined in a full matrix least-squares calculation on *F*<sup>2</sup>. Program used to solve structure and to refine structure; SHELXS97 and SHELXL97.<sup>12</sup> Molecular graphics; Ortep-3 for windows.<sup>13</sup>

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-262133). The data can be obtained free of charge via [www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi](http://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](mailto:deposit@ccdc.cam.ac.uk)).

### Synthesis.

**Dichloropentamethylcyclopentadienyl(2,4-pentanedionato)titanium(IV) (1):** To a slurry solution of [CpMe<sub>5</sub>TiCl<sub>3</sub>] (0.102 g, 0.35 mmol) in 50 mL of hexanes was added a solution of *n*-BuLi (0.14 mL, 0.35 mmol, 2.5M in hexane) under argon at -78 °C. The mixture was stirred for 20 min, and 2,4-pentanedione (36  $\mu$ L, 0.35mmol) was added. The mixture was stirred for 24 h at RT, after which a resulting brown solution was reduced in volume under reduced pressure to remove volatile materials. The residue was taken up in hexanes (20 mL) and filtered through Celite, and the filtrate was reduced in volume to 10 mL. Storing of the mixture at -30 °C gave rectangular cubes of Cp\*Ti(acac)Cl<sub>2</sub> (0.074 g, 0.21 mmol, 60%). This was then obtained as single crystals from the concentrated hexanes solution by cooling at -30 °C. IR (Nujol, cm<sup>-1</sup>) 1589 (s), 1523 (s), 1458 (m), 1366 (s), 1280 (m), 1184 (w), 1026 (m), 930 (w), 768 (w), 675 (m), 644 (s), 609 (m). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ 5.88 (CH),  $\delta$ 2.27 (s, 6H, CH<sub>3</sub> on acac),  $\delta$ 2.17 (s, 15H, CH<sub>3</sub> on Cp\*). <sup>13</sup>C NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  191.6 (CO),  $\delta$  136.4 (C<sub>5</sub>Me<sub>5</sub>),  $\delta$  101.9 (CH),  $\delta$  26.8 (CH<sub>3</sub> on acac),  $\delta$  13.7 (CH<sub>3</sub> of Cp).

**Dichloropentamethylcyclopentadienyl(1,3-diphenyl-1,3-propanedionato)titanium(IV) (2):** To a slurry solution

of  $[\text{Cp}^*\text{Me}_5\text{TiCl}_3]$  (0.102 g, 0.35 mmol) in 50 mL of hexanes was added a solution of *n*-BuLi (0.14 mL, 0.35 mmol, 2.5 M in hexane) under argon at  $-78^\circ\text{C}$ . The mixture was stirred for 20 min. and 1,3-diphenyl-1,3-propanedione (0.078 g, 0.35 mmol) was added. The mixture was stirred for 24 h at RT, after which a resulting orange solution with orange colored flocculent precipitates 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 volume of the solution was reduced to 10 mL and layering of 10 mL of hexanes to the concentrated dichloromethane solution gave rectangular cubes of  $\text{Cp}^*\text{Ti}(\text{1,3-diphenyl-1,3-propanedionato})\text{Cl}_2$  (0.105 g, 0.26 mmol, 74%). IR (Nujol,  $\text{cm}^{-1}$ ) 3055 (vw), 1589 (m), 1526 (vs), 1477 (s), 1441 (m), 1333 (s), 1300 (m), 1225 (w), 1184 (vw), 1159 (vw), 1123 (vw), 1078 (m), 1024 (m), 1001 (vw), 945 (w), 818 (w), 775 (s), 719 (m), 669 (m), 619 (vw), 608 (vw).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.11 (c, 4H, phenyl),  $\delta$  7.59 (c, 6H, phenyl),  $\delta$  7.20 (s, 1H, CH),  $\delta$  2.24 (s, 15H,  $\text{CH}_3$  on  $\text{Cp}^*$ ).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  185.0 (CO),  $\delta$  136.6,  $\delta$  133.4,  $\delta$  129.2,  $\delta$  128.4 (all phenyl carbons),  $\delta$  120.9 ( $\text{C}_5\text{Me}_5$ ),  $\delta$  93.7 (CH),  $\delta$  13.9 ( $\text{CH}_3$  on Cp).

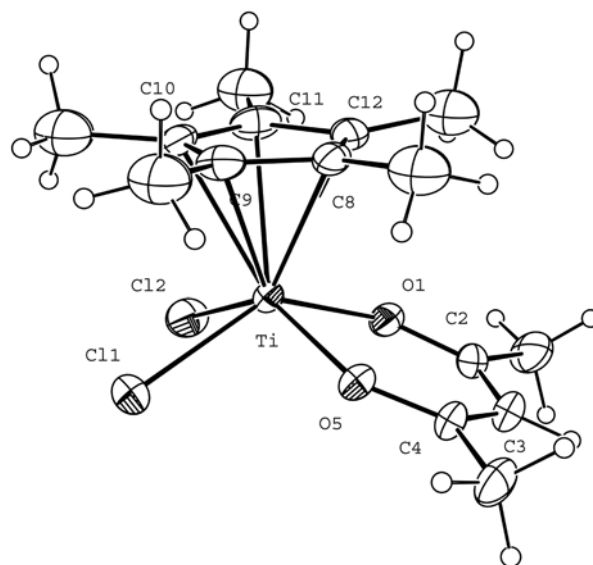
## Results and Discussion

Addition of 1 equiv. of  $\beta$ -diketone such as 2,4-pentanedione and 1,3-diphenyl-1,3-propanedione to the reaction mixture generated from  $\text{Cp}^*\text{TiCl}_3$  and 1 equiv. of *n*-BuLi in hexanes at  $-78^\circ\text{C}$  resulted in the formation of  $\text{Cp}^*(\text{acac})\text{TiCl}_2$  (**1**) and  $\text{Cp}^*\text{Ti}(\text{1,3-diphenyl-1,3-propanedionato})\text{Cl}_2$  (**2**) (Scheme 1), respectively. Complexes **1** and **2** were characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and a single-crystal X-ray diffraction analyses. The IR spectra of both **1** and **2** contained intense infrared bands between  $1500\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  suggesting that the ligand is chelated through the two keto oxygens.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complexes contain resonances responsible for the pentamethyl cyclopentadienyl group and  $\beta$ -diketonate ligands in **1** and **2**.

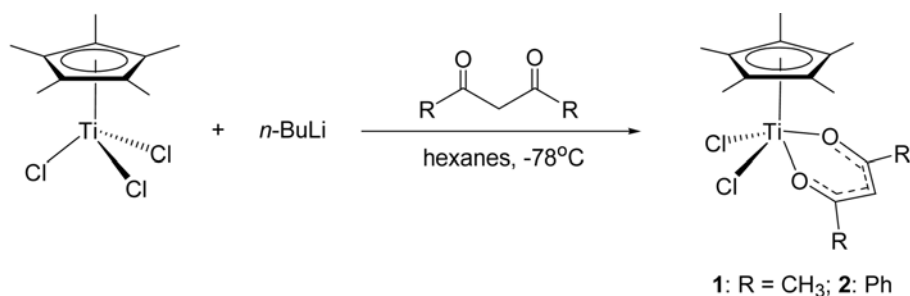
To confirm the molecular structure of complex **1**, single crystal X-ray diffraction study was performed. The data collection and structure solution parameters for **1** are given in Table 1. The molecular geometry and probability ellipsoids along with the numbering schemes are given Figure 1, and selected bond lengths and angles are listed in

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

Empirical formula	$\text{TiC}_{15}\text{H}_{22}\text{Cl}_2\text{O}_2$
FW (amu)	353.13
Crystal system	Monoclinic
Space group	$P 2_1/c$
Radiation (Mo $K\alpha$ ) ( $\lambda/\text{\AA}$ )	0.71073
a ( $\text{\AA}$ )	8.5142(17)
b ( $\text{\AA}$ )	26.235(5)
c ( $\text{\AA}$ )	8.4029(17)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	116.16(3)
$\gamma$ ( $^\circ$ )	90
V ( $\text{\AA}^3$ )	1684.7(6)
Z	4
$d_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.392
Absorption coefficient, $\mu$ ( $\text{mm}^{-1}$ )	0.823
F (0 0 0)	736
$\theta$ 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 [ $I > 2\sigma(I)$ ]	$R_1 = 0.0885$ , $wR_2 = 0.2003$
Largest diff. peak and hole ( $\text{e}\text{\AA}^{-3}$ )	0.654 and $-0.662$



**Figure 1.** ORTEP drawing of the complex **1**, showing the atom numbering scheme and 30% probability ellipsoids.



**Scheme 1**

**Table 2.** Selected bond lengths (Å) and angles (deg) for complex **1**

Ti-O(1)	1.989(5)	Ti-C(9)	2.380(8)
Ti-O(5)	2.010(5)	Ti-C(10)	2.360(7)
Ti-Cl(1)	2.340(2)	Ti-C(11)	2.378(7)
Ti-Cl(2)	2.337(2)	Ti-C(12)	2.374(7)
Ti-C(8)	2.372(7)		
O(1)-Ti-O(5)	81.1(2)	O(1)-Ti-Cl(1)	139.11(16)
O(1)-Ti-Cl(2)	82.24(16)	O(5)-Ti-Cl(1)	82.33(15)
O(5)-Ti-Cl(2)	139.43(16)	Cl(2)-Ti-Cl(1)	86.59(9)

Table 2. As illustrated in Figure 1, the molecular structure of **1** could be described as a distorted square pyramidal, with the apical position of the Cp\* ring centroid and the bidentate 2,4-pentanedione and two chloro ligands occupying the basal positions.

The bond lengths between titanium and oxygen atoms in  $\beta$ -diketonate are 1.989(5) and 2.010(5) Å in complex **1**. These values are comparable to those reported for Ti(IV) and Ti(III) complexes of CpTi(acac)Cl<sub>2</sub> (1.991(2) Å),<sup>10</sup> CpTi(2,2,6,6-tetramethyl-3,5-heptanedionato)Cl<sub>2</sub> (1.967(3) Å),<sup>10</sup> [Ti(acac)<sub>3</sub>]<sup>+</sup> (1.940(2) Å),<sup>14</sup> Ti(acac)<sub>3</sub> (2.014(5) Å),<sup>5</sup> Cp<sub>2</sub>Ti(1-phenyl-1,3-butanedionato) (2.0818(18) Å),<sup>7</sup> and Cp<sub>2</sub>Ti(1,3-diphenyl-1,3-propanedionato)Ti (2.077(4) Å).<sup>7</sup> The Ti-Cl bond lengths of 2.340(2) and 2.337(2) Å in **1** are similar to those reported in CpTi(acac)Cl<sub>2</sub> (2.340(1) Å) and CpTi(2,2,6,6-tetramethyl-3,5-heptanedionato)Cl<sub>2</sub> (2.327(2) Å and 2.336(2) Å),<sup>10</sup> however, slightly longer than those in CpTiCl<sub>3</sub> (2.201(5)-2.248(5) Å).<sup>15</sup> Because 2,4-pentanedione ligand is better  $\pi$ -donor than chloride ligand, the electron density on titanium metal in **1** is richer than that in CpTiCl<sub>3</sub>. Thus,  $\pi$ -donation from chloride to titanium is less needed in **1** and Ti-Cl distance in **1** is slightly increased. Due to the chelating of 2,4-pentanedione to Ti, the O-Ti-O angle of 81.1(2)<sup>o</sup> is smaller than that of Cl-Ti-Cl angle (86.59(9)<sup>o</sup>).

The catalytic properties of **1** and **2** complexes on the olefins have been undertaken, which will be reported separately.

**Acknowledgement.** This work was supported by a grant No. R01-2001-000-00055-0 from Korea Science and Engineering Foundation.

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