

Synthesis and Crystal Structure of Tris(1,3-diphenyl-1,3-propanedionato)Titanium(III)

Sung Kwon Kang,^{*} Samkeun Lee,^{*,†} Kyoung-Chae Seo,[†] and Sock Sung Yun

Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea

[†]Department of Applied Chemistry, Daejeon University, Daejeon 300-716, Korea

Received January 17, 2004

Key Words : Ti(III) complex, X-ray crystal structure, Jahn-Teller distortion

Group 4 metal derivatives are receiving increased attention on account of their potential applications in various areas of technology and model studies of synthetic and catalytic chemistry.¹⁻³ And the molecular structures and properties of titanium complexes of β -diketonates are of great interest in both experimental and theoretical respects.⁴⁻⁶ Recently, we have investigated the reactivities of $[\text{Cp}_2\text{M}]$ (M–Ti, Zr)^{7,8} prepared from $[\text{Cp}_2\text{TiM}]$ and $2n\text{-BuLi}$ with β -diketone. Synthesis and structural properties of Ti(III)(acac)_3 ,⁹ *cis*- $\text{CpZr(acac)}_2\text{Cl}$,¹⁰ $\text{Cp}_2(1\text{-phenyl-1,3-butanedionato})\text{Ti(III)}$ and $\text{Cp}_2(1,3\text{-diphenyl-1,3-propanedionato})\text{Ti(III)}$ ¹¹ have been reported. Catalytic study of $\text{Cp}_2(1\text{-phenyl-1,3-butanedionato})\text{Ti(III)}$ and $\text{Cp}_2(1,3\text{-diphenyl-1,3-propanedionato})\text{Ti(III)}$ and MMAO toward polymerization of ethylene have also been studied.⁵ The above synthetic studies of $[\text{Cp}_2\text{M}]$ (M–Ti, Zr) toward β -diketone suggested that new half-metallocene group 4 β -diketonate compounds could be prepared starting from CpMCl_3 (M–Ti, Zr, Hf). We wish to report the preparation and the structural characterization of tris(1,3-diphenyl-1,3-propanedionato) titanium(III) (**1**) complex.

Experimental Section

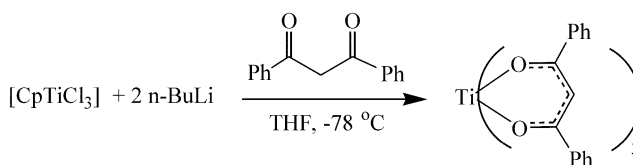
To a stirred solution of $[\text{CpTiCl}_3]$ (0.202 g, 0.92 mmol) in 20 mL of THF was added a solution of *n*-butyllithium (0.74 mL, 1.85 mmol, 2.5 M in hexane) under argon at -78°C . The mixture was stirred for 30 min. and 0.617 g (2.76 mmol) of 1,3-diphenyl-1,3-propanedione in 20 mL of THF was added and then the mixture was warmed to room temperature. After stirring for 24 h, the color of the mixture became deep blue. Volatile materials were removed under reduced pressure. The residue was taken up in 50 mL of hexanes and filtered through Celite, and the volume of the solution was reduced to 15 mL. Storing of the mixture at -30°C gave a deep blue rectangular cubes of **1** (0.414 g, 0.58 mmol, 63%). IR (Nujol cm^{-1}) 3111 (vw), 3082 (vw), 3059 (w), 1597 (w), 1582 (w), 1528 (s), 1504 (s), 1367 (s), 1315 (s), 1231 (m), 1184 (m), 1157 (w), 1065 (w), 1022 (w), 937 (w), 822 (w), 775 (m), 718 (s), 687 (m), 621 (m). The single crystals were grown from the concentrated hexanes solution of **1** by

cooling at -30°C .

The complex **1** is air sensitive material. The selected deep blue crystal was sealed into the capillary to protect from air during the X-ray data collection. The data for X-ray structure determination was collected on a Siemens P4 diffractometer equipped with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The unit cell dimensions were determined on the basis of 51 reflections in the range of $4.71^\circ < \theta < 12.53^\circ$. The data was collected by the ω - 2θ technique. Empirical absorption correction was applied to the intensity data. 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 the ideal positions and were riding on their respective carbon atoms ($B_{\text{iso}} = 1.2B_{\text{eq}}$). The structure was refined in a full matrix least-squares calculation on F^2 . All the computations were carried out with the SHELX-97 program package.¹²

Results and Discussion

Addition of 3 equiv of 1,3-diphenyl-1,3-propanedione to the reaction mixture generated from $[\text{CpTiCl}_3]$ and 2 equiv of *n*-BuLi in THF at -78°C gave a blue solution at room temperature in 24 hr. Cooling of the concentrated hot hexane solution extracted from dried blue residues gave very air-sensitive blue cubes of **1** as shown in Scheme 1. The IR spectra of both **1** show the characteristic absorption bands of phenyl groups at 3111 cm^{-1} and 3059 cm^{-1} and the presence of intense infrared bands between, 1528 cm^{-1} and 1504 cm^{-1} in **1** suggested that the ligand is chelated through the two keto oxygens. To confirm the structure of **1**, single crystal diffraction studies were performed. The data collection and structure solution parameters for complex **1** are given in Table 1. The molecular geometry and probability ellipsoids



Scheme 1. Synthesis pathway of the complex **1**.

^{*}Co-Corresponding Authors. Sung Kwon Kang (skkang@cnu.ac.kr), Samkeun Lee (lsk236@dju.ac.kr)

Table 1. Crystallographic data of Complex 1

Empirical formula	TiC ₁₅ H ₃₃ O ₆
FW (amu)	717.61
Crystal system	Triclinic
Space group	P-1
Radiation (Mo K α) ($\lambda/\text{\AA}$)	0.71073
a (\AA)	10.381(5)
b (\AA)	11.819(5)
c (\AA)	16.169(6)
α ($^\circ$)	109.04(2)
β ($^\circ$)	95.82(2)
γ ($^\circ$)	100.92(2)
V (\AA^3)	1812.7(14)
Z	2
d_{calc} (Mg m^{-3})	1.315
Absorption coefficient, μ (mm^{-1})	0.286
F(0 0 0)	746
θ range for data collection ($^\circ$)	1.88 to 25.50
Reflections collected/unique	7958/6757 [R(int) = 0.0730]
Data / restraints / parameters	6757 / 0 / 469
Goodness-of-fit on F^2	0.915
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0742^a$, $wR_2 = 0.0921^b$
Largest diff. peak and hole hole ($e\text{\AA}^{-3}$)	0.200 and -0.199

^a $R_1 = \sum |F_o - F_c| / \sum F_o$, ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^2$.

along with the numbering schemes are shown in Figure 1, and the selected bond lengths and angles are listed in Table 2. As illustrated in Figure 1, complex 1 is homoleptic titanium(III) complex with 1,3-diphenyl-1,3-propanedionate ligands and has a distorted octahedral geometry. The known zirconium complexes with the 1,3-diphenyl-1,3-propanedionate ligand are those of the tetrakis(1,3-diphenyl-1,3-propanedionato)zirconium(IV)¹³ (2) and chlorotris(1,3-

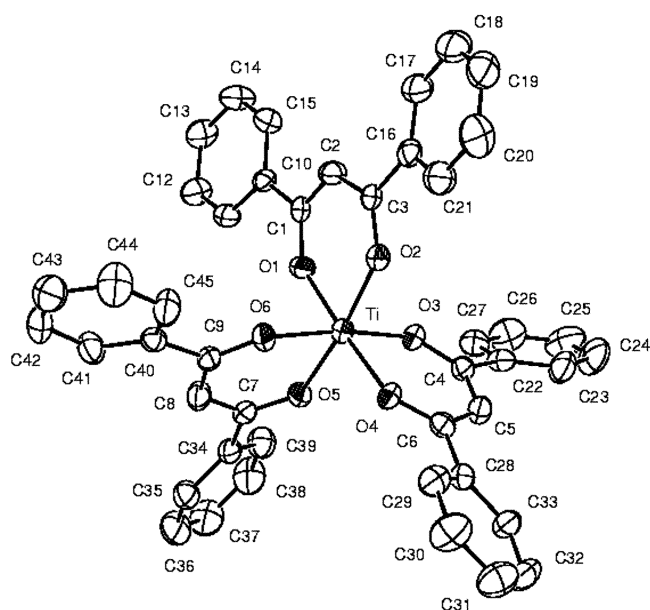


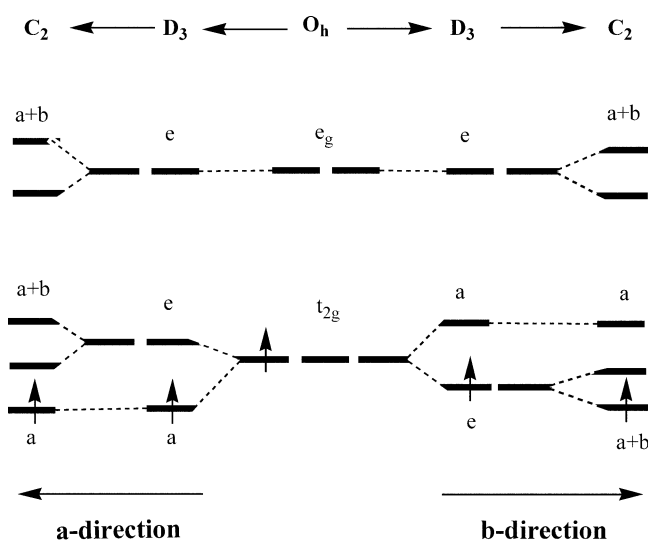
Figure 1. The molecular structure of 1, showing the atom numbering scheme and 30% probability ellipsoids. H atoms have been omitted for clarity.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for Complex 1

Ti-O(2)	1.978(3)	Ti-O(6)	2.015(4)
Ti-O(1)	1.988(3)	TiO(5)	2.022(4)
Ti-O(4)	2.010(3)	O(1)-C(1)	1.269(5)
Ti-O(3)	2.013(4)	O(2)-C(3)	1.289(5)
O(1)-Ti-O(2)	84.6(1)	O(2)-Ti-O(5)	172.5(2)
O(3)-Ti-O(4)	84.5(2)	O(1)-Ti-O(3)	92.7(2)
O(5)-Ti-O(6)	83.7(1)	O(1)-Ti-O(5)	88.1(2)
O(1)-Ti-O(4)	176.8(2)	O(1)-Ti-O(6)	90.2(2)
O(3)-Ti-O(6)	171.3(2)	O(4)-Ti-O(5)	93.5(2)

diphenyl-1,3-propanedionato)zirconium(IV)¹⁴ (3). The coordination geometry around Zr metal atom is a square antiprismatic with the eight O atoms and a capped octahedron in 2 and 3, respectively.

In general, tris(β -diketonato)titanium(III) complexes are prepared from the reaction of TiCl₃ and ammonium salt or alkali metal salt of β -diketone and these synthetic methods are a little complicated by comparison with this reports.¹⁵ And previous reports were mainly localized on the studies in elemental analysis, IR electronic spectra¹⁵ except a complex Ti(acac)₃ which has been characterized crystallographically. In recently known [Ti(acac)₃] complex,⁹ the central Ti atom is coordinated to the six oxygen atoms of acac ligands to form a distorted octahedron. The average Ti-O bond length [2.003 (3) \AA] in 1 is comparable to Ti-O bond length in [Ti(III)(acac)₃] [2.014 (5) \AA]. But the average Ti-O bond length in 1 is shorter than those of β -diketonate titanocene complexes, 2.068 (5) \AA in [Ti(η^5 -Cp)₂(acac)],⁶ 2.082 (2) \AA in [Ti(η^5 -Cp)₂(1-phenyl-1,3-butanedionato)],¹¹ and 2.077 (4) \AA in [Ti(η^5 -Cp)₂(1,3-diphenyl-1,3-propanedionato)].¹¹ On the other hand, the Ti-O bond lengths in 1 are longer than those in d⁰ system such as [Ti(acac)₃] [1.922(2)-1.956(2) \AA] with mean value of 1.940(2) \AA .¹⁰ These differences are due to the amount of electron density on titanium metal center.



Scheme 2. The qualitative distortion diagram for d¹ system from O_h to C₂ symmetry (from reference 4).

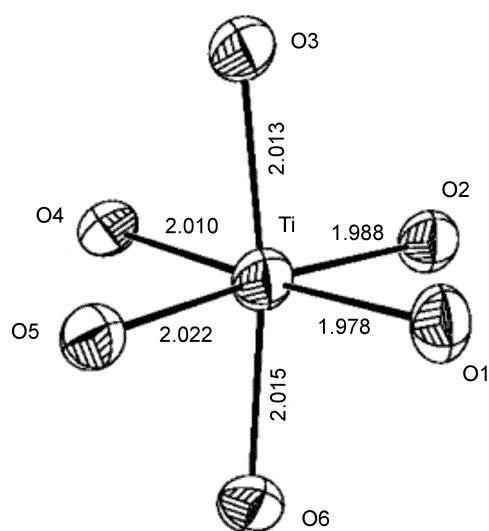


Figure 2. The molecular structure of **1** showing Jahn-Teller distortion.

The O-Ti-O angles [83.7(1)–84.6(1) $^\circ$] of chelating ligand in **1** are comparable to those for other titanium β -diketonate complexes such as [Ti(III)(acac) $_3$] with [83.3(2)–85.0(2) $^\circ$], [Ti(III)(η^5 -Cp) $_2$ (acac)] with 84.3(1) $^\circ$, [Ti(III)(η^5 -Cp) $_2$ (1-phenyl-1,3-butanedionato)] with 82.9(1) $^\circ$, [Ti(III)(η^5 -Cp) $_2$ (1,3-diphenyl-1,3-propanedionato)] with 82.6(2) $^\circ$.

As Pulay and coworkers had mentioned in their paper,⁴ Jahn-Teller distortion is expected for the partially occupied systems in the degenerated highest occupied molecular orbital (HOMO). The qualitative distortion diagram is shown on Scheme 2 for the five d orbitals of the central metal atom. For d¹ system, the distortions of both a- and b-direction will be possible to stabilize the six coordinated complexes. In b-direction, D₃ distortion will further process to C₂ symmetry to split the degenerate e orbitals into a and b orbitals. We can apply this b-direction distortion to the complex **1** which is d¹-Ti(III) system. The important atomic positions are shown on Figure 2 to display the distortion from octahedral geometry. The Ti-O1 and Ti-O2 bond lengths [1.988(4) Å and 1.978(4) Å, respectively] are obviously shorter than those of the other Ti-O bonds [2.010(4)–2.022(4) Å]. The O3-Ti-O6 angle of 171.3(2) $^\circ$ is much deviated from 180.0 $^\circ$. With the chelated 1,3-diphenyl-1,3-propanedionato ligands, geometry of complex **1** is close to C₂ symmetry than O_h or D₃.

Acknowledgement. This work was supported by a grant

No. R01-2001-000-00055-0 from Korea Science & Engineering Foundation.

Supplementary Material. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-228874). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi>. (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail:deposit@ccdc.cam.ac.uk).

References

- (a) Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Burlakov, V. V.; Shur, V. B. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 1414. (b) Kim, S.; Lee, Y.; Kang, E.; Kim, S. H.; Ko, J.; Lee, B.; Cheong, M.; Suh, I.; Kang, S. O. *Organometallics* **2003**, *22*, 3958. (c) Nii, S.; Terao, J.; Kambe, N. *J. Org. Chem.* **2004**, *69*, 573.
- Kang, S. K.; Ahn, B. G.; Choi, F. S. *Bull. Korean Chem. Soc.* **1994**, *15*, 996.
- Woo, H.-G.; Kim, B.-H.; Song, S.-J. *Bull. Korean Chem. Soc.* **1999**, *20*, 865.
- Diaz-Acosta, I.; Baker, J.; Hinton, J. E.; Pulay, P. *Spectrochim. Acta, Part A* **2003**, *59*, 363.
- (a) Lee, S.; Seo, K.; Lee, D.; Yun, S. *React. Kinet. Catal. Lett.* **2003**, *80*, 53. (b) Ganjali, M. R.; Daftari, A.; Mizani, F.; Salavati-Niasari, M. *Bull. Korean Chem. Soc.* **2003**, *24*, 23.
- Bond, A. M.; Colton, R.; Englert, U.; Hugel, H.; Marken, F. *Inorg. Chim. Acta* **1995**, *235*, 117.
- (a) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 394. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (c) Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924.
- Morita, K.-I.; Nishiyama, Y.; Ishii, Y. *Organometallics* **1993**, *12*, 3748.
- Yun, S. S.; Suh, I.; Choi, S.; Kim, T.; Lee, S. *J. Coord. Chem.* **1999**, *47*, 315.
- Yun, S.-S.; Suh, I.-L.; Kim, E.-H.; Lee, S. *J. Korean Chem. Soc.* **1999**, *43*, 593.
- Yun, S. S.; Suh, I.; Kim, E.; Lee, S. *J. Coord. Chem.* **2000**, *51*, 219.
- Sheldrick, G. M. *SHELXS97 and SHELXL97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
- Chun, H. K.; Steffen, W. L.; Fay, R. C. *Inorg. Chem.* **1979**, *18*, 2458.
- Janiak, C.; Scharmann, T. G. *Acta Cryst.* **1998**, *C54*, 210.
- (a) Boiko, A. I.; Lobanov, F. I.; Opasova, R. G.; Savranskii, I. I. *Koordinatsionnaya Khimiya* **1990**, *16*, 780. (b) Yurchenko, E. N.; Avdeev, V. I.; Shugam, E. A. *Teoreticheskaya i Eksperimental'naya Khimiya* **1970**, *6*, 84. (c) Chakravarti, B. N. *Naturwiss.* **1958**, *45*, 286. (d) Barnum, D. W. *J. Inorg. Nucl. Chem.* **1961**, *21*, 22.
- Thewalt, U.; Adam, T. Z. *Naturforsch.* **1978**, *33b*, 142.