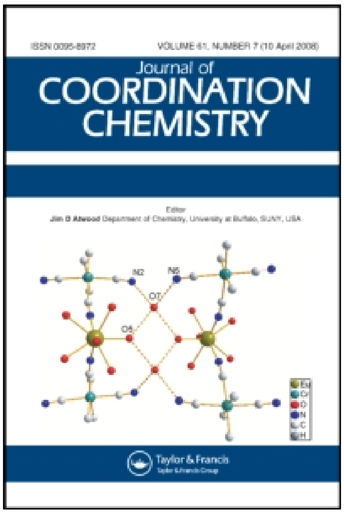


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and crystal structures of dichlorocyclopentadienyl β-diketonate titanium complexes

Samkeun Lee[a]; Kyoung-Chae Seo[a]; Sock Sung Yun[b]; Sung Kwon Kang[b]
[a] Department of Chemistry, Daejeon University, Daejeon 300-716, Korea [b] Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea

To cite this Article Lee, Samkeun , Seo, Kyoung-Chae , Yun, Sock Sung and Kang, Sung Kwon(2005) 'Synthesis and crystal structures of dichlorocyclopentadienyl β-diketonate titanium complexes', Journal of Coordination Chemistry, 58: 8, 695 — 700

To link to this Article: DOI: 10.1080/00958970500055476

URL: http://dx.doi.org/10.1080/00958970500055476

Journal of Coordination Chemistry
Vol. 58, No. 8, 20 May 2005, 695–700

Synthesis and crystal structures of dichlorocyclopentadienyl *β*-diketonate titanium complexes

SAMKEUN LEE†*, KYOUNG-CHAE SEO†, SOCK SUNG YUN‡
and SUNG KWON KANG‡*

†Department of Chemistry, Daejeon University, Daejeon 300-716, Korea
‡Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea

(*Received 3 May 2004; in final form 19 January 2004*)

Complexes of acetylacetonatodichlorocyclopentadienyltitanium(IV) (**1**) and dichlorocyclopentadienyl(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV) (**2**) have been prepared and their crystal structures determined by X-ray diffraction methods. Complex **1** crystallizes in space group $P2_1/m$ with $a = 7.1893(10)$, $b = 11.7680(17)$, $c = 7.6129(11)$ Å, $\beta = 109.901(12)^\circ$; complex **2** crystallizes in space group $P2_1/n$ with $a = 10.065(2)$, $b = 16.322(3)$, $c = 12.219(2)$ Å, $\beta = 110.99(3)^\circ$. The molecular structures of **1** and **2** can be described as square-based pyramidal, with the centroid of the C_5H_5 ring occupying the apical site and the bidentate β-diketonate and two chloride ligands occupying the basal positions. The average distances between titanium and oxygen atoms are 1.991(2) and 1.967(3) Å in compounds **1** and **2**, respectively.

Keywords: Titanium(IV) complex; β-Diketonate; Cyclopentadienyl; Crystal structure

1. Introduction

The synthesis of β-diketonate complexes of titanium(IV) generally involves the reaction of Cp_2TiCl_2 with β-diketones in the presence of amine, or with the sodium salt of a β-diketone [1], or by protonolysis of $C_5Me_5TiMe_3$ with β-diketone [2]. Recently, we investigated the reactivities of Cp_2M (M = Ti, Zr) [3,4], prepared from Cp_2MCl_2 and 2*n*BuLi, towards β-diketone providing Ti(III)(acac)$_3$ [5], *cis*-CpZr(acac)$_2$Cl [6], Cp_2(1-phenyl-1,3-butanedionato)Ti(III) and Cp_2(1,3-diphenyl-1,3-propanedionato)Ti(III) [7]. Catalytic studies of Cp_2(1-phenyl-1,3-butanedionato)Ti(III) and Cp_2(1,3-diphenyl-1,3-propanedionato)Ti(III) and MMAO towards polymerization of ethylene have also been studied [8]. Reactions of Cp_2M (M = Ti, Zr) with β-diketone suggested that new half-metallocene β-diketonate compounds could be prepared starting from $CpMCl_3$ (M = Ti, Zr, Hf). We report here the preparation and the structural characterization

---

*Corresponding author. Email: lsk236@dju.ac.kr; skkang@cnu.ac.kr

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500055476

of half-sandwich dichloro β-diketonate titanium complexes, CpTi(β-diketonato)Cl_2 (β-diketonato = acac, 2,2,6,6-tetramethyl-3,5-heptanedionato).

2. Experimental

2.1. *Synthesis of acetylacetonatodichlorocyclopentadienyltitanium(IV) (1)*

To a slurry of $CpTiCl_3$ (0.22 g, 1.00 mmol) in 30 mL of hexanes was added a solution of *n*BuLi (0.40 mL, 1.00 mmol, 2.5 M in hexane) under argon at −78°C. The mixture was stirred for 30 min and 100 µL (1.00 mmol) of 2,4-pentanedione was added and then the mixture was warmed to room temperature and stirred. After stirring for 5 h, the color of the mixture turned orange. Volatile materials were removed under reduced pressure. The residue was taken up in 30 mL of CH_2Cl_2, filtered through Celite, and the volume of the solution was reduced to 10 mL. Layering of 10 mL of hexanes to the concentrated solution gave rectangular cubes of **1** (0.22 g, 0.75 mmol, 75%). NMR spectra of **1** were recorded on a Bruker AC-300 instrument: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.69 (s, 5H, C_5H_5), 5.95 (s, 1H, C*H*), 2.18 (s, 6H, CH_3); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 187.9 (O*C*), 119.2 (C_5H_5), 99.6 (*C*H), 21.2 (CH_3). Infrared spectra of **1** were recorded on a Shimadzu FT-IR 8300 spectrophotometer (4000–400 cm^{-1}) in Nujol mull.

2.2. *Synthesis of dichlorocyclopentadienyl(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium(IV) (2)*

To a slurry solution of $CpTiCl_3$ (0.206 g, 0.94 mmol) in 30 mL of hexanes was added a solution of *n*BuLi (0.38 mL, 0.95 mmol, 2.5 M in hexane) under argon at −78°C. The mixture was stirred for 20 min and 198 µL (0.95 mmol) of 2,2,6,6-tetramethyl-3,5-heptanedione was added and the mixture was warmed to room temperature. After stirring for 1 h, the color of the mixture turned orange. Volatile materials were removed under reduced pressure. The residue was taken up in 10 mL of ether, filtered through Celite, and the volume of the solution was reduced to 10 mL. Layering of 10 mL of hexanes to the concentrated solution gave rectangular cubes of **2** (0.17 g, 0.46 mmol, 49%). NMR spectra of **2** were recorded on a Bruker AC-300 instrument: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.68 (s, 5H, C_5H_5), 6.22 (C*H*), 1.26 (s, 18H, CH_3); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 202.8 (*C*O), 123.6 (C_5H_5), 94.3 (*C*H), 41.2 (CMe_3), 27.7 (CMe_3). Infrared spectra of **2** were recorded on a Shimadzu FT-IR 8300 spectrophotometer (4000–400 cm^{-1}) in Nujol mull.

2.3. *Crystal structure determination*

The data for X-ray structure determination were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The unit cell dimensions were determined on the basis of 51 reflections in the range of $4.5^\circ < \theta < 12.7^\circ$ for **1** and 25 reflections with $11.3^\circ < \theta < 13.7^\circ$ for **2**. The data were collected by the ω–2θ technique. The standard direct method was used to position the heavy atoms. The remaining nonhydrogen atoms were located from the subsequent difference Fourier syntheses. All nonhydrogen atoms were refined anisotropically.

All hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms ($B_{\mathrm{iso}} = 1.2B_{\mathrm{eq}}$ and $1.5B_{\mathrm{eq}}$). The structure was refined by a full-matrix least-squares calculation on F^2. The programs used to solve and refine the structures were SHELXS97 and SHELXL97 [9] and ORTEP-3 for windows was used for the molecular graphics [10].

2.4. *Crystal data*

$C_{10}H_{12}Cl_2O_2Ti$ (**1**), Monoclinic, $P2_1/m$, $a = 7.1893(10)$, $b = 11.7680(17)$, $c = 7.6129(11)$ Å, $\beta = 109.901(12)°$, $V = 605.62(15)$ Å^3, $D_c = 1.552\ \mathrm{g\,cm^{-3}}$, $Z = 2$, $R = 0.0457$, $wR = 0.0879$, $F(000) = 288$, $\mu(\mathrm{Mo\,K\alpha}) = 1.124\ \mathrm{mm^{-1}}$, $(\Delta\rho)\mathrm{max} = 0.322$, $(\Delta\rho)\mathrm{min} = -0.326$ e Å^{-3}.

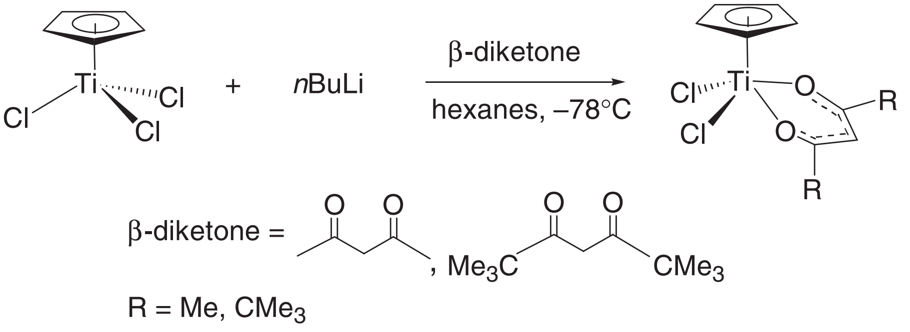
$C_{16}H_{24}Cl_2O_2Ti$ (**2**), Monoclinic, $P2_1/n$, $a = 10.065(2)$, $b = 16.322(3)$, $c = 12.219(2)$ Å, $\beta = 110.99(3)°$, $V = 1874.1(7)$ Å^3, $D_c = 1.301\ \mathrm{g\,cm^{-3}}$, $Z = 4$, $R = 0.0645$, $wR = 0.1714$, $F(000) = 768$, $\mu(\mathrm{Mo\,K\alpha}) = 0.743\ \mathrm{mm^{-1}}$, $(\Delta\rho)\mathrm{max} = 0.603$, $(\Delta\rho)\mathrm{min} = -0.597$ e Å^{-3}.

3. Results and discussion

3.1. *Synthesis and general characterization*

Addition of 1 equiv of a β-diketone such as 2,4-pentanedione or 2,2,6,6-tetramethyl-3,5-heptanedione to the reaction mixture generated from $CpTiCl_3$ and 1 equiv of *n*BuLi in hexanes at −78°C gave an orange solution. Recrystallization of the orange complex by layering hexanes to the concentrated CH_2Cl_2 extracts or ether extracts yielded single crystals of **1** and **2**, respectively (scheme 1). When the reaction was performed in THF, a blue solution was produced. Addition of 1 or 5 equiv of 2,4-pentanedione to the reaction mixture generated from $CpTiCl_3$ and 1 or 2 equiv of *n*BuLi in THF at −78°C gave a blue solution. Recrystallization of the blue compound by cooling the hexane extracts at −30°C gave $Ti(III)(acac)_3$ [5], which was characterized by a single-crystal diffraction study and IR. In the case of 2,2,6,6-tetramethyl-3,5-heptanedione, intractable blue materials were formed.

The IR spectra of both **1** and **2** contain C–H stretching frequencies at 3105 and 3109 $\mathrm{cm^{-1}}$, respectively, from the η^5-cyclopentadienyl groups. The presence of intense infrared bands between 1500 and 1600 $\mathrm{cm^{-1}}$ in **1** and **2** suggest that the ligand is chelated through the two keto oxygens. ^{1}H and ^{13}C NMR spectra of the compounds



Scheme 1.

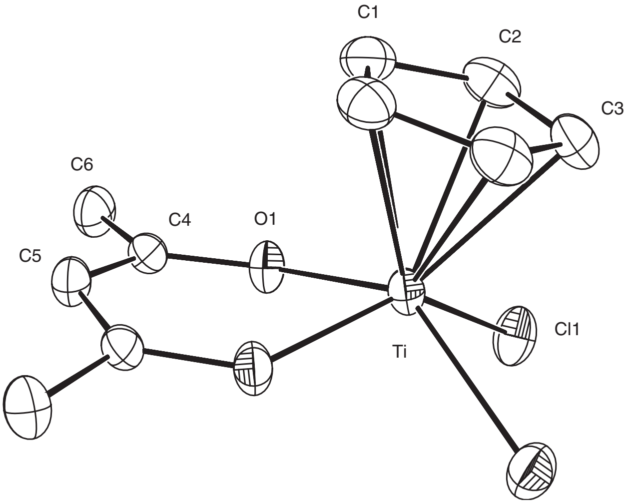


Figure 1. The molecular structure of **1**, showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

contain resonances for the cyclopentadienyl group and β-diketonate ligands in **1** and **2**. To confirm the structure of complexes **1** and **2**, single-crystal X-ray diffraction studies were performed.

3.2. *Descriptions of crystal structures*

The molecular geometry and thermal ellipsoids along with the atom numbering schemes are shown in figures 1 and 2, and selected bond distances and angles are listed in tables 1 and 2 for complexes **1** and **2**, respectively. The solid-state structure of **1** is constrained by a crystallographic mirror plane that bisects the O–Ti–O and Cl–Ti–Cl bond angles and passes through atoms C(3), Ti and C(5). The molecular structures of **1** and **2** could be described as square-based pyramidal, with the centroid of the C_5H_5 ring occupying the apical site and the bidentate β-diketonato and two chloride ligands occupying the basal positions.

The average distances between titanium and oxygen atoms are 1.991(2) and 1.967(3) Å in **1** and **2**, respectively. These values are comparable to those reported for Ti(IV) and Ti(III) complexes such as $[Ti(acac)_3]^+$ [1.940(2) Å] [11], $[Ti(acac)_3]$ [2.014(5) Å] [5], $[Cp_2Ti$(1-phenyl-1,3-butanedionato)] [2.0818(18) Å] [7] and $[Cp_2Ti$(1,3-diphenyl-1,3-propanedionato)Ti] [2.077(4) Å] [7]. The Ti–Cl bond distances of 2.340(1) Å in **1** and 2.327(2) and 2.336(2) Å in **2** are slightly longer than those in $CpTiCl_3$ [2.201(5)–2.248(5) Å] [12]. Because the β-diketonate ligand is a better π-donor than the chloride ligand, the electron density on titanium in **1** and **2** is richer than that in $CpTiCl_3$. Thus, less π-donation from chloride to titanium is needed in **1** and **2** and the Ti–Cl distance in **1** and **2** increases. The O–Ti–O angles of about 80° are smaller than those of the Cl–Ti–Cl angles [86.16(5) and 87.85(7)° for **1** and **2**, respectively] because of chelate bonding to the Ti atoms. Reactions of various β-diketones with other group 4 half-metallocene complexes generated from $CpMCl_3$ ($M = Zr, Hf$) and *n*BuLi have been undertaken, giving different kinds of β-diketonate complexes, which will be reported separately.

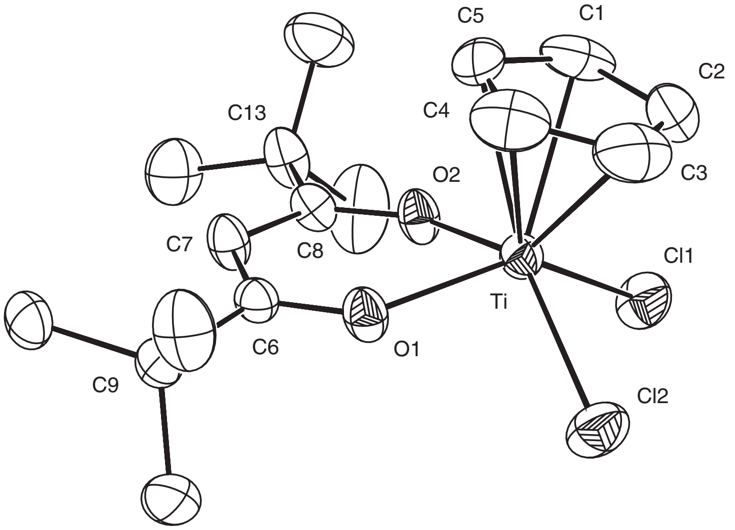


Figure 2. The molecular structure of **2**, showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **1**.

Ti–O(1)	1.991(2)	O(1)–C(4)	1.287(3)
Ti–C(3)	2.315(4)	C(1)–C(2)	1.394(4)
Ti–Cl(1)	2.340(1)	C(2)–C(3)	1.395(4)
Ti–C(2)	2.349(3)	C(4)–C(5)	1.392(4)
Ti–C(1)	2.384(3)	C(4)–C(6)	1.489(4)
O(1)–Ti–O(1)#1	80.73(11)	C(4)–C(5)–C(4)#1	121.8(4)
O(1)–C(4)–C(5)	122.1(3)	Cl(1)–Ti–Cl(1)#1	86.16(5)

Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, z.

Table 2. Selected bond lengths (Å) and angles (°) for **2**.

Ti–O(2)	1.953(3)	O(1)–C(6)	1.266(5)
Ti–O(1)	1.981(3)	O(2)–C(8)	1.275(6)
Ti–C(5)	2.319(6)	C(1)–C(2)	1.378(9)
Ti–C(1)	2.324(6)	C(1)–C(5)	1.390(9)
Ti–Cl(1)	2.327(2)	C(2)–C(3)	1.347(10)
Ti–C(4)	2.333(7)	C(3)–C(4)	1.335(10)
Ti–Cl(2)	2.336(2)	C(4)–C(5)	1.328(10)
Ti–C(3)	2.358(6)	C(6)–C(7)	1.386(6)
Ti–C(2)	2.359(6)	C(7)–C(8)	1.392(6)
		C(8)–C(13)	1.518(7)
O(2)–Ti–O(1)	80.34(13)	C(6)–C(7)–C(8)	120.9(5)
Cl(1)–Ti–Cl(2)	87.85(7)	O(2)–C(8)–C(7)	121.9(4)
O(1)–C(6)–C(7)	122.5(4)		

Supplementary material

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 234652 and 234653. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by grant no. R01-2001-000-00055-0 from the Korea Science and Engineering Foundation and a grant (2003–2004) from Chungnam National University.

References

[1] R. Martin-Nentino, R. Jimenez-Aparicio, M.C. Barral, *J. Organomet. Chem.*, **269**, 267 (1984), and references cited therein.
[2] P. Gómez-Sal, A. Martín, M. Mena, P. Royo, R. Serrano, *J. Organomet. Chem.*, **419**, 77 (1991).
[3] L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt, B. Wolf, *Angew. Chem., Int. Ed. Engl.*, **24**, 394 (1985). (b) E. Negishi, F.E. Cederbaum, T. Takahashi, *Tetrahedron Lett.*, **27**, 2829 (1986). (c) J.Y. Corey, X.-H. Zhu, T.C. Bedard, L.D. Lange, *Organometallics*, **10**, 924 (1991).
[4] K.-I. Morita, Y. Nishiyama, Y. Ishii, *Organometallics*, **12**, 3748 (1993).
[5] S.-S. Yun, I.-L. Suh, S.-S. Choi, T.-H. Kim, S. Lee, *J. Coord. Chem.*, **47**, 315 (1999).
[6] S.-S. Yun, I.-L. Suh, E.-H. Kim, S. Lee, *J. Korean Chem. Soc.*, **43**, 593 (1999).
[7] S.-S. Yun, I.-L. Suh, E.-H. Kim, S. Lee, *J. Coord. Chem.*, **51**, 219 (2000).
[8] S.-S. Yun, K.-C. Seo, D.-K. Lee, S. Lee, *React. Kinet. Catal. Lett.*, **80**, 53 (2003).
[9] G.M. Sheldrick, *SHELXS97: Program for Structure Resolution*, University of Göttingen, Germany (1997); *SHELXL97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[10] L.J. Farrugia, *J. Appl. Cryst.*, **30**, 565 (1997).
[11] U. Thewalt, T.Z. Adam, *Naturforscher*, **33b**, 142 (1978).
[12] R.D. Rogers, M.M. Benning, L.K. Kurihara, K.J. Moriarty, M.D. Rausch, *J. Organomet. Chem.*, **293**, 51 (1985).