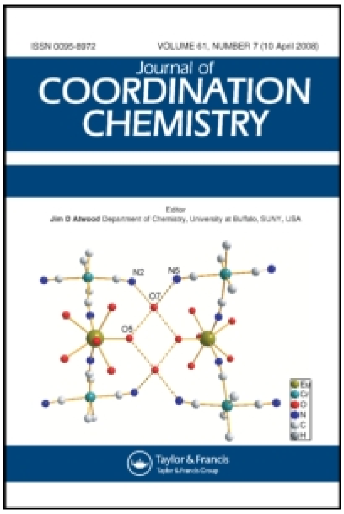

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Note

ALTERNATIVE SYNTHESIS AND CRYSTAL STRUCTURES OF TITANOCENE(III)-β-DIKETONATE COMPLEXES

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Reaction of titanocene prepared from Cp_2TiCl_2 and $2n$-BuLi with β-diketones (β-diketone = 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, 3-methyl-2,4-pentanedione or 3-ethyl-2,4-pentanedione) afforded the titanocene(III) β-diketonate complex. The compounds $[Ti(\eta^5\text{-}Cp)_2(\text{1-phenyl-1,3-butanedionate})]$ and $[Ti(\eta^5\text{-}Cp)_2(\text{1,3-diphenyl-1,3-propanedionate})]$ have been characterized by X-ray crystallography.

Keywords: Metallocene; titanocene; crystal structure; β-diketonate complex

Owing to catalytic activities of group 4 metallocenes such as with the polymerization of various olefins,[1] reactivities have been extensively studied. Other catalytic reactions effected by organometallic compounds of group 4 elements are the hydrogenation and isomerization of olefins,[2] the cyclo-oligomerization of dienes,[3] and the ring opening polymerization of strained cyclic olefins.[4]

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In the course of studying the reactivity of group 4 metallocene compounds, we have shown that the reaction of phenylacetaldehyde with catalytic amounts of "CP_2M" (M = Ti, Zr) prepared from the Cp_2MCl_2 (M = Ti, Zr) with 2 equiv. of *n*-BuLi produces spectroscopically pure 5-benzyl-1,3-dihydroxy-2,4-diphenyl pyran as a single isomer in good yield (60%), which could be assumed to represent the formal trimerization of phenylacetaldehyde.[5] We also have shown an alternative route to the formation of the tris(acetylacetonato)titanium(III) complex from the reaction of 2,4-pentanedione with "Cp_2Ti" (**1**), prepared from the Cp_2TiCl_2 with 2 equiv. of *n*-BuLi, and have reported its single crystal structure (1).[6] When a sterically bulky β-diketone is allowed to react with **1**, a different titanium(III)-β-diketonate complex was formed.

Here we wish to report an alternative synthesis of titanocene(III)-β-diketonate complexes from the reaction of **1** and β-diketones (β-diketone = 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, 3-methyl-2,4-pentanedione, and 3-ethyl-2,4-pentanedione) and the single crystal structures of [(η^5-Cp)$_2$(1-phenyl-1,3-butanedionato)Ti(III)] (**2**) and [(η^5-Cp)$_2$(1,3-diphenyl-1,3-propanedionato)Ti(III)] (**3**) (2).

Addition of 1 equiv. of β-diketone (β-diketone = 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, 3-methyl-2,4-pentanedione and 3-ethyl-2,4-pentanedione) to **1** prepared from [Cp_2TiCl_2] and 2 equiv. of *n*-BuLi in THF at −78°C gives a deep blue solution at room temperature in 24 h.[†] Cooling of the concentrated hot hexane solution extracted from dried blue residues gives very air-sensitive greenish blue cubes of titanocene(III)-β-diketonate complexes, which were characterized spectroscopically and

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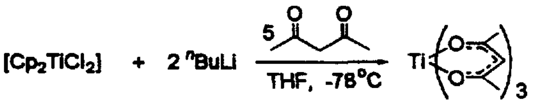
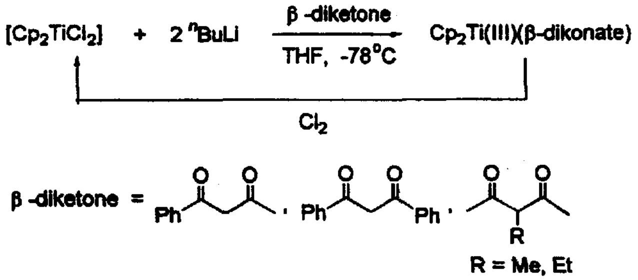
[†] Compound **2**: slow addition of 1-phenyl-1,3-butanedione (0.65 g, 4.0 mmol) to the reaction mixture prepared from [Cp_2TiCl_2] (1.00 g, 4.0 mmol) and *n*-butyllithium (5 cm^3 of 1.6 M, 8.0 mmol) in THF (80 cm^3) at −78°C gives a colour change to deep blue in 24 h. Cooling of the concentrated deep blue hexane solution extracted from residues after removing volatiles from the reaction mixture affords dark blue cubes of **2** (0.75 g, 2.20 mmol, 55%); MS(FAB): *m*/*z* 339 M^+; IR (Nujol): ν 3080 (w), 1591 (vs), 1568 (s), 1514 (s), 1485 (s), 1450 (s), 1359 (sh), 1288 (m), 1211 (m), 1170 (m), 1107 (m), 1012 (s), 960 (m), 846 (m), 783 (s), 759 (s), 712 (vs), 687 (s), 583 (s), 536 (s), 424 (s) cm^{-1}. Compound **3**: This was similarly prepared, yield; 41%; MS(FAB): *m*/*z* 401 M^+; IR (Nujol): ν 3060 (w), 1596 (w), 1519 (s), 1465 (vs), 1375 (s), 1338 (m), 1290 (m), 1224 (m), 1066 (m), 1024 (m), 783 (w), 759 (s), 719 (s), 687 (s), 621 (s), 519 (w) cm^{-1}. [Ti(η^5-Cp)$_2$(3-methyl-acac)] and [Ti(η^5-Cp)$_2$(3-ethyl-acac)] were also similarly prepared. For [Ti(η^5-Cp)$_2$(3-methylacac)], yield; 20%); MS(FAB): *m*/*z* 291 M^+; IR (Nujol): ν 3090 (w), 3070 (w), 1589 (s), 1551 (vw), 1522 (w), 1464 (vs), 1377 (m), 1358 (vw), 1288 (m), 1175 (w), 1161 (w), 1070 (w), 1015 (w), 978 (s), 891 (w), 804 (m), 791 (m), 770 (vw), 721 (s), 656 (m), 444 (m), 401 (m) cm^{-1}. For [Ti(η^5Cp)$_2$(3-ethyl-acac)], yield; 28%; MS(FAB): *m*/*z* 305 M^+; IR (Nujol): ν 3100 (w), 1585 (m), 1547 (s), 1460 (vs), 1377 (m), 1354 (s), 1339 (s), 1315 (s), 1283 (s), 1259 (m), 1173 (m), 1094 (w), 1063 (m), 997 (s), 951 (w), 908 (s), 789 (m), 704 (s), 679 (m), 569 (m), 444 (m), 428 (w) cm^{-1}.

chemically. Reaction of the titanocene(III)-β-diketonate complexes with 1 equiv. of chlorine gas gives $[\mathrm{Ti}(\eta^5\text{-Cp})_2\mathrm{Cl}]_2$ quantitatively (2).



(1)



(2)

Single crystal diffraction studies for **2** and **3** were performed.[‡] Figures 1 and 2 show perspective views of **2** and **3** along with selected bond distances and angles.[8] The Cp–Ti–Cp angle in **2** and **3** is 135.64(19) and 134.27(17), respectively, close to that in titanocene(III).[7] The average distance Ti–C in **2** and **3** is 2.383(5) and 2.364(7) Å, respectively, similar to the value obtained for other titanocene(III)[7] and titanocene(IV)[8] compounds. However, the mean value of Ti–O in **2** and **3** is 2.081(18) (4) and 2.077(4) Å, respectively, and is ~0.01 Å longer than that in $[\mathrm{Ti}(\eta^5\text{-Cp})_2(\mathrm{acac})]$,[9] and ~0.12 Å longer in $[\mathrm{Ti(acac)}_3]$.[6] The O1–Ti–O2 angle of 82.99(7) and 82.55(15) in **2** and **3** is smaller than the value of 85–88° evaluated by Prout *et al.*[10] The longer distances of Ti–O and smaller angles of O1–Ti–O2 in **2** and **3** can be explained by the sterically bulky phenyl group.

Titanocene(III)-β-diketonate complexes usually have been prepared by replacement of one chloride ligand in $[\mathrm{Ti(III)}(\eta^5\text{-Cp})_2\mathrm{Cl}]_2$ with diketonate,

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[‡] Compound **2**: Cooling of the deep blue hexane solution of **2** at −30°C afforded a dark blue crystal suitable for diffraction studies. X-ray data: monoclinic ($P2_1/c$) with $a = 10.4601(9)$, $b = 7.881(2)$, $c = 21.058(2)$ Å, $\beta = 100.500(7)°$, $V = 1706.9(5)$ Å^3, $d_{\mathrm{calcd.}} = 1.320\,\mathrm{g\,cm^{-3}}$, $Z = 4$ and $T = 23$°C. Details are available in the supplementary material. Compound **3**: Cooling of the deep blue hexane solution of **3** at −30°C afforded a dark blue crystal suitable for diffraction studies. X-ray data: monoclinic ($P2_1$/c) with $a = 15.692(5)$, $b = 8.0403(11)$, $c = 15.711(3)$ Å, $\beta = 91.350(18)°$, $V = 1981.7(7)$ Å^3, $d_{\mathrm{calcd.}} = 1.345\,\mathrm{g\,cm^{-3}}$, $Z = 4$ and $T = 18(2)$°C. Details are available in the supplementary material.

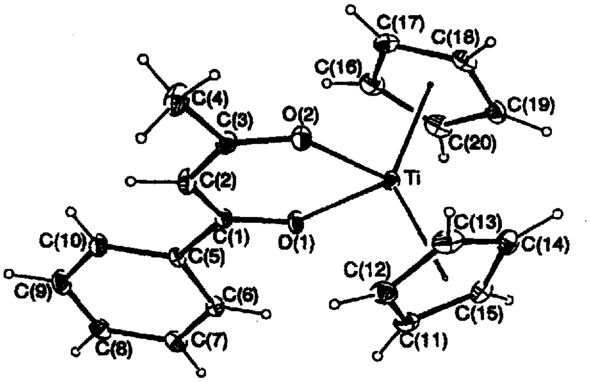

FIGURE 1 ORTEP drawing of 2. Selected bond distances (Å) and angles (deg): Ti–O1 2.0774(17), Ti–O2 2.0839(19), Ti–C11 2.424(3), Ti–C12 2.379(3), Ti–C13 2.348(3), Ti–C14 2.365(3), Ti–C15 2.401(3), Ti–C16 2.389(3), Ti–C17 2.414(3), Ti–C18 2.381(3), Ti–C19 2.361(3), Ti–C20 2.358(3), Ti–Cp1 2.071(4), Ti–Cp2 2.072(4), Cp1–Ti–Cp2 135.64(19), O1–Ti–O2 82.99(6).

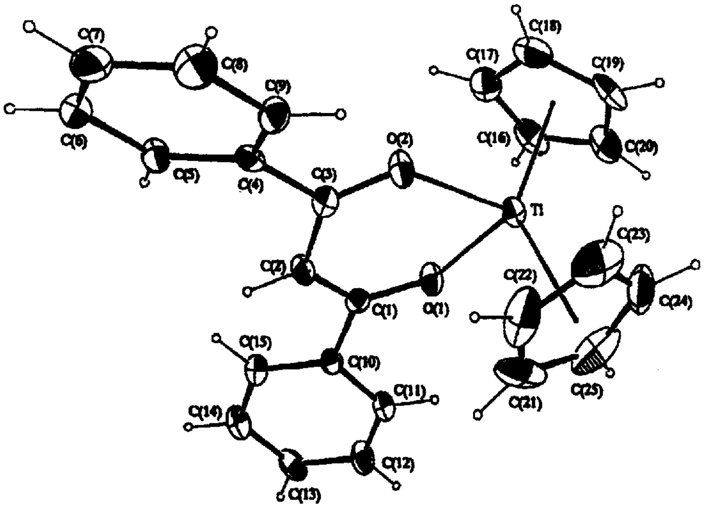

FIGURE 2 ORTEP drawing of 3. Selected bond distances (Å) and angles (deg): Ti–O1 2.087(4), Ti–O2 2.067(4), Ti–C16 2.372(6), Ti–C17 2.339(7), Ti–C18 2.358(7), Ti–C19 2.375(6), Ti–C20 2.399(6), Ti–C21 2.364(9), Ti–C22 2.383(8), Ti–C23 2.349(8), Ti–C24 2.350(8), Ti–C25 2.341(9), Ti–Cp1 2.060(3), Ti–Cp2 2.064(6), Cp1–Ti–Cp2 134.27(17), O1–Ti–O2 82.55(15).

and can be produced by the reduction of $[Ti(\eta^5\text{-}Cp)_2Cl_2]$.[11] Recently a procedure employing $[Co(\eta^5\text{-}Cp)_2][Ti(\eta^5\text{-}Cp)_2Cl_2]$[12] generated from $[Ti(\eta^5\text{-}Cp)_2Cl_2]$ and cobaltocene was reported.[9] Addition of β-diketones to $[Co(\eta^5\text{-}Cp)_2][Ti(\eta^5\text{-}Cp)_2Cl_2]$ in the presence of triethylamine and

$NEt_3HSO_3CF_3$ in THF at ambient temperatures produces titanocene(III)-β-diketonate complexes.[9] Both of these methods are complicated compared with this report. The reactions of various β-diketones with other group 4 metallocenes such as zirconone and hafnocene generated from the reaction of $[Cp_2MCl_2]$ ($M = Zr, Hf$) and *n*-BuLi have been undertaken. They give different kinds of β-diketonate complexes, which will be reported separately.

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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