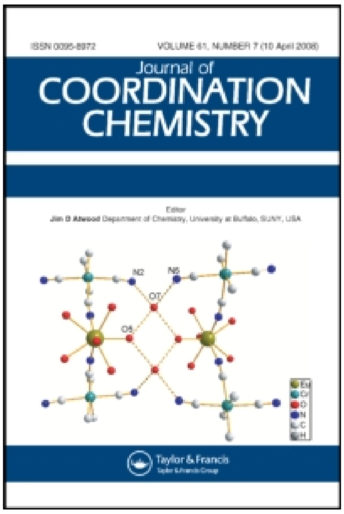

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Sock Sung Yun[a]; Il-Hwan Suh[b]; Sung-San Choi[b]; Tae-Hun Kim[a]; Samkeun Lee[c]
[a] Department of Chemistry, Chungnam National University, Taejon, South Korea [b] Department of Physics, Chungnam National University, Taejon, South Korea [c] Department of Chemistry, Taejon University, Taejon, South Korea

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Note

ALTERNATIVE FORMATION AND CRYSTAL STRUCTURE OF TRIS(ACETYLACETONATO)TITANIUM(III) FROM TITANOCENE AND 2,4-PENTANEDIONE

SOCK SUNG YUN[a,*], IL-HWAN SUH[b], SUNG-SAN CHOI[b],
TAE-HUN KIM[a] and SAMKEUN LEE[c]

[a]*Department of Chemistry,* [b]*Department of Physics, Chungnam National University, Taejon, 305-764, South Korea;* [c]*Department of Chemistry, Taejon University, Taejon 300-716, South Korea*

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An alternative route to the formation of tris(acetylacetonato)titanium(III) has been found in the course of studying the reactivity of Cp_2Ti toward 2,4-pentanedione. The crystal structure of tris(acetylacetonato)titanium(III) has been determined.

Keywords: Metallocene; titanocene; crystal structure; tris(acetylacetonato)titanium(III)

Organometallic compounds of early transition elements have an important role in the development of both synthetic organometallic and catalytic chemistry.[1,2] It has long been known that group 4 metallocene derivatives have interesting catalytic activities in the polymerization of various olefins.[3] Other catalytic reactions effected by organometallic compounds of group 4 elements are the hydrogenation and isomerization of olefins,[4] the cyclooligomerization of dienes,[5] and the ring opening polymerization of strained cyclic

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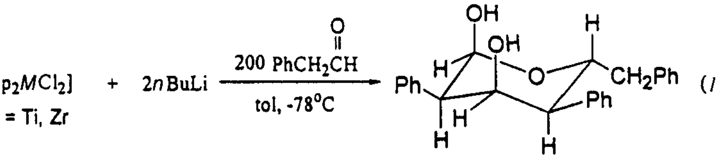
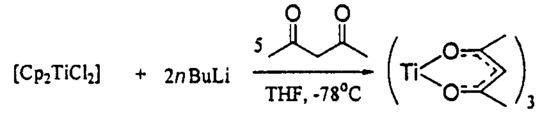
* Corresponding author.

olefins.[6] We have shown that the addition of 200 equiv of phenylacetaldehyde to the solution of Cp_2M prepared from the Cp_2MCl_2 (M = Ti, Zr) with 2 equiv of *n*-BuLi in toluene at −78°C produced white solids at room temperature in 24 h, and simple filtration gives spectroscopically pure 5-benzyl-1,3-dihydroxy-2,4-diphenyl pyran as the single isomer of double aldol reaction-product of phenylacetaldehyde (65%).[7] (*1*)



(*1*)



(2)

In the course of studying the reactivity of Cp_2Ti (**1**) toward 2,4-pentanedione, tris(acetylacetonato)titanium(III) (**2**) which has the potential as a catalyst for the acetylene polymerization[8] was unprecedentedly formed (*2*). We wish to report the alternative route to the formation and single crystal structure of **2**. Addition of 1 to 5 equiv of 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 blue cubes of **2**. When 5 equiv of 2,4-pentanedione is used, the highest yield of **2** is obtained (60%); **2** has been previously prepared from the reaction of the ammonium salt of acetylacetate and $TiCl_3$, but characterized only by elemental analysis, IR and EPR.[9] A single-crystal diffraction studies of **2** was performed and Figure 1 shows a perspective view of **2** along with selected bond distances and angles.[‡] The six oxygen atoms coordinating titanium form a slightly distorted octahedron, and Ti–O ranges from 1.984(9) to 2.030(8) Å with a mean value of 2.000(9) Å, ~0.06 Å longer than

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[†] Typical experimental procedure: Slow addition of 2,4-pentanedione ($0.66\,\mathrm{cm}^3$, 6.43 mmol) to the reaction mixture prepared from $[Cp_2TiCl_2]$ (0.32 g, 1.29 mmol) and *n*-butyllithium ($1.61\,\mathrm{cm}^3$ of 1.6 M, 2.58 mmol) in THF ($5\,\mathrm{cm}^3$) 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** (0.26 g, 0.75 mmol, 58%).

[‡] Cooling of the deep blue hexane solution of **2** at −30 °C afforded dark blue crystals suitable for diffraction studies. X-ray data for **2**: monoclinic, space group $P2_1/c$ with $a = 14.187(4)$, $b = 7.576(3)$, $c = 16.574(7)$ Å, $\beta = 99.34(2)°$, $V = 1757.8(11)\,\text{Å}^3$, $d_{\mathrm{calcd}} = 1.305\,\mathrm{g\,cm^{-3}}$, $Z = 4$, $T = 25°\mathrm{C}$. Details are available in the supplementary material.

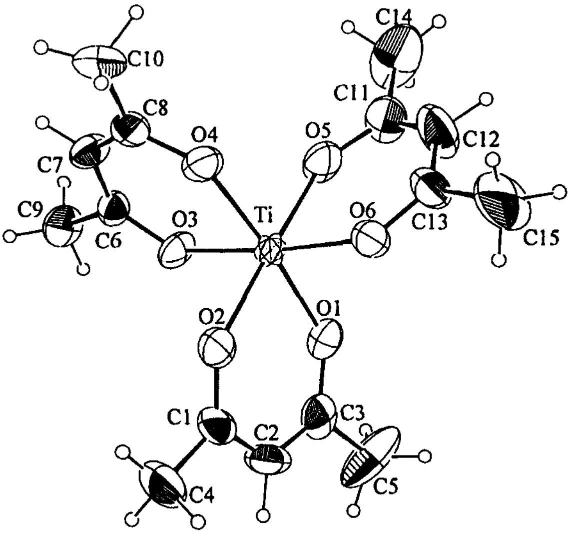

FIGURE 1 ORTEP drawing of **2**. Selected bond distances (Å) and angles (deg): Ti–O1 1.99(9), Ti–O2 2.013(8), Ti–O3 2.030(8), Ti–O4 1.992(10), Ti–O5 1.984(9), Ti–O6 1.989(8), O1–Ti–O2 83.0(4), O1–Ti–O3 92.7(3), O1–Ti–O4 175.2(4), O1–Ti–O5 95.6(4), O1–Ti–O6 89.8(4).

in $[Ti(acac)_3]^+$, the cation complex of titanium(IV).[10] GC-mass spectra of the volatiles of the reaction mixture distilled at 10^{-4} mmHg do not contain cyclopentadiene or its dimer.

The mechanistic details of the reaction remain unclear. However, the formation of **2** from **1** and 2,4-pentanedione most probably proceeds due to the oxophilicity of titanium metal centre in **1**. Efforts to elucidate the mechanism for the formation, the reaction pathway responsible for **2** and the seperation of organic products of the reaction are currently in progress.

Acknowledgements

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Supplementary Material

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

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