

# Synthesis of 1-Methyl-3-aryl-substituted Titanocene and Zirconocene Dichlorides and Crystal Structure of Bis[ $\eta^5$ -1-methyl-3-( $\alpha$ , $\alpha$ -dimethylbenzyl)cyclopentadienyl]titanium Dichloride

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The syntheses of a series of 1-methyl-3-aryl-substituted titanocene and zirconocene dichlorides are reported. These complexes are synthesized by the reaction of 2- and 3-methyl-6, 6-dimethylfulvenes (1:4) with aryllithium, followed by the reaction with  $\text{TiCl}_4 \cdot 2\text{THF}$ ,  $\text{ZrCl}_4$  and  $(\text{CpTiCl}_2)_2\text{O}$  respectively, to give complexes 1—5. The complex [ $\eta^5$ -1-methyl-3-( $\alpha$ ,  $\alpha$ -dimethylbenzyl)cyclopentadienyl]titanium dichloride has been studied by X-ray diffraction. The red crystal of this complex is monoclinic, space group  $P2_1/C$  with unit cell parameters:  $a = 6.973(6) \times 10^{-1} \text{ nm}$ ,  $b = 36.91(2) \times 10^{-1} \text{ nm}$ ,  $c = 10.063(4) \times 10^{-1} \text{ nm}$ ,  $\alpha = \beta = \gamma = 93.35(5)^\circ$ ,  $V = 2584(5) \times 10^{-3} \text{ nm}^3$  and  $Z = 4$ . Refinement for 1004 observed reflections gives the final  $R$  of 0.088. There are four independent molecules per unit cell.

**Keywords** Titanocene complex, zirconocene complex, crystal structure

## Introduction

During the past two decades, the synthesis of substituted titanocene and zirconocene complexes has been intensively studied, because of the importance of such complexes as catalyst in olefin polymerization. The different metallocene complexes with a variety and a num-

ber of substituents on the Cp ring differ greatly in catalytic activity and selectivity in olefin polymerization.<sup>1</sup> It was reported that a  $C_2$ -symmetric ansa-metallocenes with a Si-atom bridging the two ligands, due to higher stereorigidity and favorable electronic characteristics, had higher polymerization activities than unbridged metallocenes, making propylene polymerization with higher MW and isotacticity.<sup>2,3</sup> One of the recent efforts has been directed toward the synthesis of sterically di- or tri-substituted titanocene and zirconocene complexes.<sup>4</sup> In the past few years, the research in this group has dealt with the chemistry of substituted titanocene and zirconocene complexes.<sup>5</sup> In this paper we wish to report the synthesis of some new 1, 3-disubstituted titanocene and zirconocene complexes and the molecular structure of one of such typical compounds.

## Results and discussion

The following synthetic routes shown in Scheme 1 were used for preparation of 1-methyl-3-aryl-substituted titanocene and zirconocene dichlorides.

In order to synthesize 1-methyl-3-aryl-substituted titanocene and zirconocene dichlorides we prepared 2-

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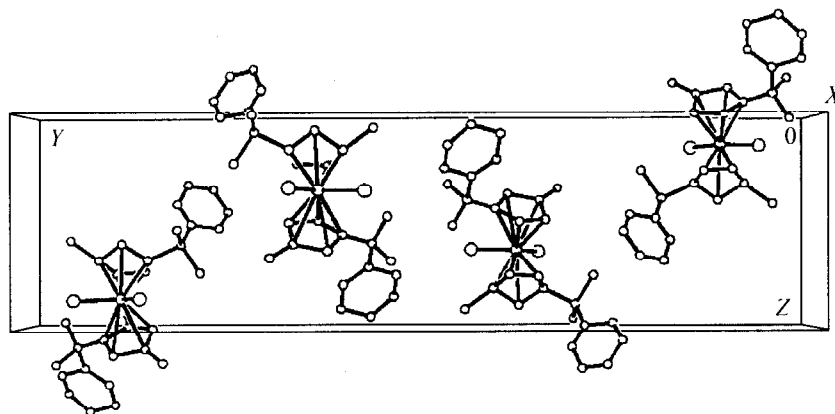


Fig. 2 Elemental cell of 1.

ture and the elemental cell of 1 is shown in Fig. 1 and Fig. 2, respectively. Its crystal data, selected bond lengths and bond angles are listed in Table 1, and Table 2 respectively.

Table 1 Crystal data of 1

Chemical formula	$C_{30}H_{34}Cl_2Ti/513.41$
Color	Red
Crystal size	$0.1 \times 0.2 \times 0.3$
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ (nm)	$6.973(6) \times 10^{-1}$
$b$ (nm)	$36.91(2) \times 10^{-1}$
$c$ (nm)	$10.063(4) \times 10^{-1}$
$\alpha = \beta = \gamma$ ( $^\circ$ )	93.35(5)
$V$ (nm <sup>3</sup> )	$2584(5) \times 10^{-3}$
$Z$	4
$D_c$ (Mg/m <sup>3</sup> )	1.32
Absorption coefficient (mm <sup>-1</sup> )	0.551
$F(000)$	1080
$\lambda$ (nm)(Mo $K_\alpha$ )	0.71073
Scan Type	$\omega/2\theta$
$\theta$ range ( $^\circ$ )	2.0—23.0
Scan speed ( $^\circ$ /min)	0.92—5.49
Reflections collected	3893
Independent reflections	3515 ( $R_{int} = 7.6\%$ )
Observed reflections	1004 ( $I \geq 3\sigma(I)$ )
Final $R$ and $R_w$	0.088 and 0.097
Good-of-fit	3.1

## Experimental

All experiments were carried out under argon. All solvents were purified and distilled freshly before use. <sup>1</sup>H NMR spectra were determined on a Bruker Ac-300 spectrometer using tetramethylsilane as internal standard. IR spectra were recorded on a Shimadzu IR-435

spectrometer. Measurement of mass spectra was carried out on an HP-5988 mass-spectrometer. X-ray diffraction was carried out on an Enraf-Nonius CAD<sub>4</sub> diffractometer. Melting points were uncorrected.  $TiCl_4 \cdot 2THF$  was synthesized according to the method of Ref. 6. 2, 6, 6-(3, 6, 6)-trimethylfulvene was prepared according to Ref. 7, Bp = 36—39 $^\circ$ C/2mm, yield = 51.6—62.5%. The ratio of 2, 6, 6-trimethylfulvene to 3, 6, 6-isomer was = 1:4 (on GC).

### Synthesis of 1-methyl-2(3)-(α, α-dimethyl)benzyl cyclopentadienyl lithium

The solution of trimethylfulvene (9.5 g, 70 mmol) in ether was added dropwise into a solution of phenyl lithium (70 mmol) in ether with stirring at 0 $^\circ$ C. It was stirred for 5 h at room temperature and filtrated. The resulting white solid was washed with petroleum ether (20 mL  $\times$  2), dissolved in dried THF (120 mL) and titrated with standard HCl. Yield = 62%.

### Synthesis of compound 1

Into a solution of  $TiCl_4 \cdot 2THF$  (2.5 g, 8.0 mmol) in THF (20 mL), above lithium salt solution (55 mL, 16 mmol) was added dropwise. The reaction solution darkened from yellow to red and dark red. It was stirred overnight at rt and worked up with 6N hydrochloric acid (20 mL). Then ether (50 mL) was added, the organic layer was separated, washed with saturated NaCl aqueous solution (30 mL  $\times$  2), dried with anhydrous  $CaCl_2$ , and filtrated. After the organic solution was concentrated to 10—15 mL, petroleum ether (20 mL) was added. Then this solution was kept in refrigerator, and a red

solid was formed. After recrystallization with toluene and petroleum ether 2.26 g of target product as a red crystal was obtained. Yield = 55.1%. mp = 215–217°C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.18–7.24 (m, 10H), 6.59 (m, 2H), 6.03 (s, 2H), 4.91 (s, 2H), 2.21 (s, 6H), 1.60 (s, 12H).  $\nu_{\text{max}}$  (KBr): 3380, 2955, 1488, 1428, 1376, 848, 766, 694 cm<sup>-1</sup>.  $m/z$  (%): 477 (M – Cl, 29), 442 (M – 2Cl, 34), 315 (M – Cp, 16), 280 (M – Cp' – Cl, 41), 245 ((M – Cp' – 2Cl, 11). Anal. C<sub>30</sub>H<sub>34</sub>Cl<sub>2</sub>Ti. Calcd: C, 70.18; H, 6.67. Found: C, 70.14; H, 6.77.

#### Synthesis of compound 2

By using a corresponding fulvene as starting material, compound 2 was synthesized in the same way as compound 1. A red solid was obtained, yield = 28.4%. mp = 209–211°C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.08 (s, 8H), 6.58 (m, 2H), 6.03 (m, 2H), 4.96 (m, 2H), 2.30 (s, 6H), 2.22 (s, 6H), 1.58 (s, 6H), 1.57 (s, 6H).  $\nu_{\text{max}}$  (KBr): 3399, 3072, 2951, 1505, 1461, 1430, 1376, 846, 813 cm<sup>-1</sup>.  $m/z$  (%): 505 (M – Cl, 21), 470 (M – 2Cl, 23), 329 (M – Cp', 16), 294 (M – Cp' – 2Cl, 35), 259 (M – Cp' – 2Cl, 7). Anal. C<sub>32</sub>H<sub>38</sub>Cl<sub>2</sub>Ti. Calcd: C, 70.99; H, 7.07. Found: C, 70.99; H, 7.05.

#### Synthesis of compound 3

By using the above procedure, ZrCl<sub>4</sub> was used instead of TiCl<sub>4</sub>, and compound 3 as a white solid was synthesized, yield = 25.2%, mp = 198–200°C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.18–7.23 (m, 10H), 6.36 (m, 2H), 5.88 (m, 2H), 4.99 (m, 2H), 2.21 (s, 6H), 1.66 (s, 6H), 1.60 (s, 6H).  $\nu_{\text{max}}$  (KBr): 3390, 3070, 2958, 1488, 1438, 1376, 845, 766 cm<sup>-1</sup>.  $m/z$  (%): 359 (M – Cp, 74), 324 (M – Cp' – Cl, 2), 197 (Cp', 24). Anal. C<sub>30</sub>H<sub>34</sub>Cl<sub>2</sub>Zr. Calcd: C, 64.72; H, 6.16. Found: C, 64.67; H, 5.98.

#### Synthesis of compound 4

Compound 4 was obtained by using the same procedure as compound 3, white solid, yield = 21.4%. mp = 192–193°C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.08 (s, 8H), 6.35 (m, 2H), 5.87 (m, 2H), 5.01 (m, 2H), 2.31 (s, 6H),

2.21 (s, 6H), 1.65 (s, 6H), 1.57 (s, 6H).  $\nu_{\text{max}}$  (KBr): 3391, 3078, 2956, 1495, 1473, 1376, 849, 811 cm<sup>-1</sup>.  $m/z$  (%): 373 (M – Cp', 100), 338 (M – Cp' – Cl, 2). Anal. C<sub>32</sub>H<sub>38</sub>Cl<sub>2</sub>Zr. Calcd: C, 65.57; H, 6.55. Found: C, 65.34; H, 6.54.

#### Synthesis of compound 5

To a solution of (CpTiCl<sub>2</sub>)<sub>2</sub>O (2.2 g, 10 mmol) in THF (20 mL), 1-methyl-2(3)-(α, α-dimethyl)-4'-methyl benzyl cyclopentadienyl lithium salt (20 mL, 10 mmol) in ether was added dropwise at 0°C. It was stirred for 20 h, 6N hydrochloric acid (20 mL) was added, then ether (50 mL) was added. The organic layer was separated and washed with saturated NaCl aqueous solution (30 mL × 2), dried with anhydrous CaCl<sub>2</sub>, and concentrated to 10–15 mL, petroleum ether (20 mL) was added, then the organic solution was kept in refrigerator. A red solid was formed. After recrystallization from toluene and petroleum, 1.5 g of target product was obtained. Yield = 38%. mp = 189–190°C.  $\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.21–7.19 (m, 4H), 6.60 (m, H), 6.48 (m, H), 6.21 (s, 5H), 6.06 (m, H), 2.34 (s, 3H), 2.21 (s, 3H), 1.67 (s, 3H), 1.65 (s, 3H).  $\nu_{\text{max}}$  (KBr): 3388, 3079, 2954, 1613, 1494, 1462, 1354, 1184, 848, 719 cm<sup>-1</sup>.  $m/z$  (%): 359 (M – Cl, 32), 329 (M – Cp, 100), 294 (M – Cp – Cl, 29), 183 (M – Cp', 24), 148 ((M – Cp' – Cl, 27). Anal. C<sub>21</sub>H<sub>24</sub>Cl<sub>2</sub>Ti. Calcd: C, 63.82; H, 6.12. Found: C, 63.47; H, 6.23.

**Table 2** Selected bond lengths and bond angles of 1

Atoms		Bond length (10 <sup>-1</sup> nm)
Ti	Cl(1)	2.330(5)
Ti	Cl(2)	2.357(5)
Ti	C(11)	2.43(2)
Ti	C(12)	2.57(2)
Ti	C(13)	2.55(3)
Ti	C(14)	2.31(1)
Ti	C(15)	2.39(1)
Ti	C(31)	2.30(2)
Ti	C(32)	2.55(2)
Ti	C(33)	2.30(2)
Ti	C(34)	2.18(2)
Ti	C(35)	2.29(2)
C(1)	C(13)	1.58(3)
C(2)	C(33)	1.55(2)

continued

Atoms		Bond angles (°)	
Cl(1)	Ti	Cl(2)	90.4(2)
Cl(1)	Ti	C(11)	84.5(4)
Cl(1)	Ti	C(12)	82.0(3)
Cl(1)	Ti	C(13)	111.7(5)
Cl(1)	Ti	C(14)	137.7(5)
Cl(1)	Ti	C(15)	114.7(4)
Cl(2)	Ti	C(31)	78.4(5)
Cl(2)	Ti	C(32)	83.6(3)
Cl(2)	Ti	C(33)	113.8(4)
Cl(2)	Ti	C(34)	137.9(4)
Cl(2)	Ti	C(35)	112.2(4)
Ti	C(13)	C(1)	128(1)
Ti	C(33)	C(2)	140(1)

## References

- (a) Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.  
(b) Kaminsky, W.; Arudt, M. *Advances in Polymer Science*, Vol. 127, Springer-Verlag, New York, **1997**, pp. 143-187.  
(c) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175.  
(d) Huang, J.; Rempel, G, L. *Prog. Polym. Sci.* Vol. 20, **1995**, pp. 459—526.
- Spaleck, W.; Kuber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954 and references therein.
- Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem. Int. Ed. Engl.*, **1990**, *29*, 279.
- (a) Hughes, R. P.; Kowalski, A. S.; Lompfrey, J. R.; Rheingold, A. L., *Organometallics* **1994**, *13*, 2691.  
(b) Uno, M.; Ando, K.; Komatsuzaki, N.; Tsuda, T.; Tanaka, T.; Sawada, M.; Takahashi, S. *J. Organomet. Chem.* **1994**, *473*, 303.  
(c) Clark, T. J.; Killian, C. M.; Luthra, S.; Nile, T. A. *J. Organomet. Chem.* **1993**, *462*, 247.
- (a) Qian, Y.; Huang, J.; Yang, J.; Chan, A. S. C.; Chen, W.; Chen, X.; Li, G.; Jin, X.; Yang, Q. *J. Organomet. Chem.* **1997**, *547*, 263.  
(b) Qian, Y.; Huang, J.; Huang, T.; Chen, S. *Transition Met. Chem.* **1996**, *21*, 393.  
(c) Qian, Y.; Huang, J. *Macromolecular Symp.* **1996**, *105*, 205.  
(d) Qian, Y.; Huang, J.; Chen, X.; Li, G.; Chen, W.; Li, B.; Jin, X.; Yang, Q. *Polyhedron* **1994**, *13*, 1105.
- Samuel, E.; Setton, R. *J. Organomet. Chem.* **1965**, *4*, 156.
- Besanco, J.; Top. S. *J. Organomet. Chem.* **1977**, *127*, 139.

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