

# Synthesis of functionalised titanocene complexes

Ming Zhang<sup>a\*</sup>, Ai-Qin Zhang<sup>b</sup>, Huan-Huan Chen<sup>a</sup>, Jun Chen<sup>a</sup> and Hai-Yan Chen<sup>a</sup>

<sup>a</sup>College of Chemistry, Jiangxi Normal University, Yaohu Campus, Nanchang, Jiangxi 330022, China

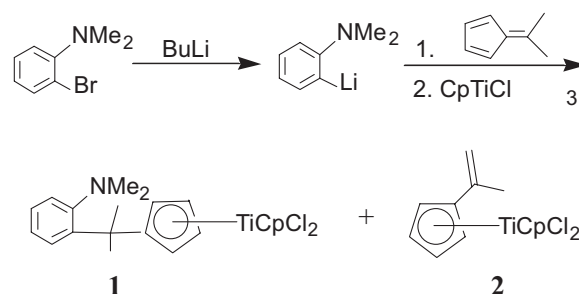
<sup>b</sup>Department of Environmental and Chemical Engineering, Nanchang Institute of Aeronautical Technology, Nanchang, Jiangxi, China

Two functionalised titanocene complexes were synthesised from fulvene as starting material.

**Keywords:** titanocene complexes, fulvene, synthesis

Many kinds of titanium and zirconium complexes have been synthesised<sup>1</sup> due to their various usages in many processes, such as: polymerisation,<sup>2</sup> hydrogenation,<sup>3</sup> isomerisation,<sup>4</sup> asymmetric Mannich-type reaction,<sup>5</sup> dinitrogen activation,<sup>6</sup> Petasis methylation reaction,<sup>7</sup> reactions with acid chlorides and 1,4-diketones.<sup>8</sup> Among the previously reported titanium complexes, titanocene derivatives can furnish structurally unique complexes. Recently, Gansauer<sup>1c</sup> reported a modular and efficient method for synthesis of cyclic complexes by treating titanocene dichloride derivatives bearing an ester group in the ligand with  $\text{ZnCl}_2$  at room temperature. Functionalised titanocene complexes were used in polymerisation, *e.g.*, half-sandwich titanocene complexes with ketimide ligands were used as catalysts in ethylene polymerisation and ethylene/norbornene copolymerisation<sup>9a</sup> and N–O chelated monocyclopentadienyl titanium complexes were used as catalysts in ethylene polymerisation,<sup>9b</sup> which shows that ligands with nitrogen have advantages in polymerisation. We report herein synthesis of two nitrogen functionalised titanocene complexes from fulvene as starting material.

*o*-Dimethylaminophenyl lithium was allowed to react with 6,6-dimethyl fulvene, then further to react with  $\text{CpTiCl}_3$ . The product was a mixture of **1** and **2**, which was indicated by  $^1\text{H}$  NMR and MS analysis (Scheme 1). The *o*-dimethylaminophenyl lithium is either a nucleophilic reagent or a base with big steric hindrance, so the products of reaction of *o*-dimethylaminophenyl lithium with 6,6-dimethyl fulvene comprise of the desired adduct product **1** and undesired elimination product **2**. The solvent in the reaction of *o*-dimethylaminophenyl lithium with 6,6-dimethyl fulvene has a big influence on the ratio of **1** and **2**. When the

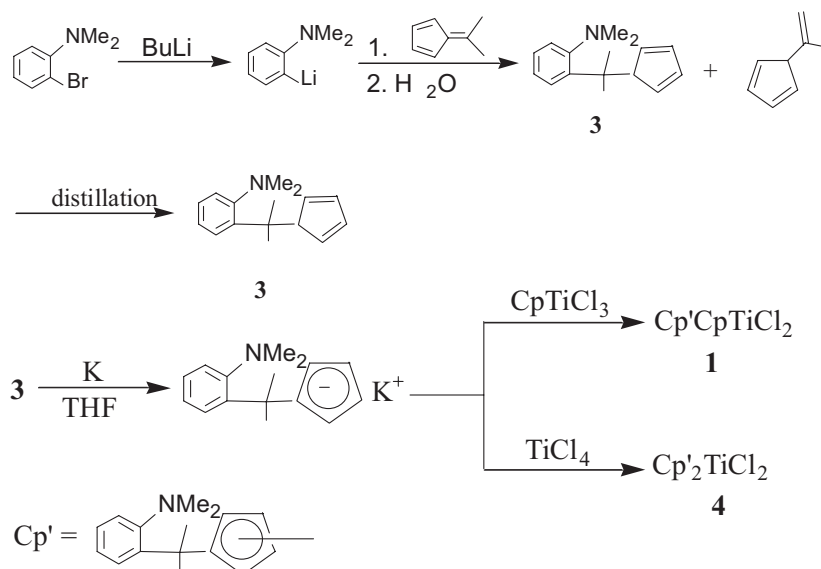


Scheme 1

solvent is THF, the ratio of **1** to **2** is 1 : 3. When the solvent is  $\text{Et}_2\text{O}$ , the ratio of **1** to **2** is 1 : 1. Hexane, benzene, toluene and dichloromethane are not suitable as solvent in this reaction due to the poor solubility of *o*-dimethylaminophenyl lithium in them. We selected  $\text{Et}_2\text{O}$  as solvent in the reaction of *o*-dimethylaminophenyl lithium with 6,6-dimethyl fulvene.

It is difficult to separate **1** and **2**. To obtain pure complex **1**, we separated the ligand **3** by distillation after hydrolysis of the lithium mixture. The potassium salt of ligand **3** was obtained by reaction of ligand **3** with potassium. Then two nitrogen functionalised titanocene complexes **1** and **4** (Scheme 2) were synthesised by reaction of potassium salt of ligand **3** with monocyclopentadienyl titanium trichloride and titanium tetrachloride respectively. They were well characterised by  $^1\text{H}$  NMR, IR, MS and elemental analysis.

In conclusion, we have provided a method for synthesis of nitrogen functionalised titanocene complexes from fulvene as starting material.



Scheme 2

\* Correspondent. E-mail: zmchem@163.com

## Experimental

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Melting points were uncorrected.  $^1\text{H}$  NMR spectra were recorded on a GERMINI-300 spectrometer using  $\text{CDCl}_3$  as solvent and  $\text{Me}_4\text{Si}$  as an internal standard. IR spectra were measured on a NICOLET MAGNA-IR550 spectrometer. MS were obtained on a HP5989A Mass Spectrometer.

**Synthesis of ligand 3:** A solution of BuLi (20.3N, 135 mmol) in hexane (66.5 ml) was added dropwise to a solution of o-bromo N, N-dimethylaniline (27 g, 135 mmol) in hexane (80 ml) with stirring at room temperature. After addition, the mixture was stirred for 2 h. The precipitate obtained was filtered then dissolved in  $\text{Et}_2\text{O}$  (150 ml). To this solution, a solution of 6, 6-dimethyl fulvene (16 g, 135 mmol) in hexane (40 ml) was added. After addition, the solution was stirred for 2 h. 100 ml of water was then added and the reaction mixture was then extracted with  $\text{Et}_2\text{O}$ . The ethereal solution was dried over  $\text{K}_2\text{CO}_3$  and the solvent were removed by vacuum. The resulting oil was then vacuum distilled (b.p.  $95^\circ\text{C}$  at 133.3 Pa) to yield 7 g of pale yellow viscous oil **3** (23% yield).  $^1\text{H}$  NMR ( $\delta$  ppm): 6.8–7.3 (m, 4H), 5.8–6.3 (m, 3H), 2.7–2.9 (m, 2H), 2.2 (s, 6H), 1.6 (s, 6H). Anal. Calc. for  $\text{C}_{16}\text{H}_{21}\text{N}$ : C, 84.6; H, 9.25; N, 6.2. Found: C, 84.3; H, 9.1; N, 6.45.

**Synthesis of 1:** A solution of **1** (2 g, 8.8 mmol) in THF (5 ml) was added to a suspension of potassium (0.356 g, 8.8 mmol) in THF (9 ml). The resulting mixture was stirred for 2 h, to give the potassium salt of the ligand. In another Schlenk flask, a solution of  $\text{CpTiCl}_3$  (1.6 g, 7.3 mmol) in THF (15 ml) was added. To this solution, the above salt of ligand solution was added with stirring. And the resulting solution was stirred for 4 h. After the solvent was removed, the residue was recrystallised from  $\text{CHCl}_3$  to afford 1.5 g of purple crystalline solid in 39% yield, m.p.  $169\text{--}171^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\delta$  ppm): 7.11–7.40 (m, 4H), 6.49 (m, 5H), 6.31 (m, 2H), 6.59 (m, 2H), 2.21 (s, 6H), 1.83 (s, 6H). IR (KBr,  $\text{cm}^{-1}$ ): 3066, 2972, 2666, 1599, 1485, 1440, 1459, 1200, 1078, 1047, 1014, 867, 818, 761. MS ( $m/e$ ): 374 (M-Cl, 4). Anal. Calc. for  $\text{C}_{21}\text{H}_{25}\text{Cl}_2\text{NTi}$ : C, 61.5; H, 6.1; N, 3.4. Found: C, 61.5; H, 6.2; N, 3.3.

**Synthesis of 4:** A solution of **1** (2.64 g, 11.6 mmol) in THF (7 ml) was added to a suspension of potassium (0.4536, 11.6 mmol) in THF

(12 ml) and the mixture was stirred for 2 h at room temperature. To this reaction mixture, a solution of  $\text{TiCl}_4$  (0.45 ml, 4.1 mmol) in benzene (1 ml) was added and the solution was stirred for 3 h. After the solvent was removed, the residue was recrystallised from  $\text{CHCl}_3$  to afford 0.32 g of purple needles in 14% yield, m.p.  $156\text{--}158^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\delta$  ppm): 7.16–7.61 (m, 8H), 6.65 (m, 4H), 6.35 (m, 4H), 2.26 (s, 12H), 2.03 (m, 12H). IR (KBr,  $\text{cm}^{-1}$ ): 3110, 2940, 2780, 1480, 1020, 940, 820, 780. MS ( $m/e$ ): 535 (M-Cl, 14.59). Anal. Calc. for  $\text{C}_{32}\text{H}_{40}\text{Cl}_2\text{N}_2\text{Ti}$ : C, 67.25; H, 7.0; N, 4.9. Found: C, 66.9; H, 7.2; N, 4.7.

Received 15 June 2007; accepted 3 September 2007

Paper 07/4703 doi: 10.3184/030823407X244887

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