APPLIED ORGANOMETALLIC CHEMISTRY
*Appl. Organometal. Chem.* 2005; **19**: 621–626
Materials, Nanoscience and Catalysis **AOC**

# Titanium(IV) complexes containing mono-cyclopentadienyl and bulky trityloxy mixed ligands: synthesis and polymerization activity

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Received 28 September 2004; Revised 27 October 2004; Accepted 3 November 2004

**Eight new $R^1CpTiCl_2(OC(C_6H_4R^2)Ph_2)$ complexes were synthesized by the reaction of $R^1CpTiCl_3$ with $Ph_2(R^2C_6H_4)COH$ ($R^2C_6H_4$ =phenyl or *o*-methyl-phenyl) in the presence of $Et_3N$ in good yield and characterized by $^1H$ NMR, elemental analysis, IR and mass spectrometry. A suitable single crystal of complex 2 ($R^1$: $CH_3$, $R^2$: H) was obtained and the structure determined by X-ray diffraction. When activated by methylaluminoxane (MAO), all complexes were active for the polymerization of ethylene and styrene. The effect of variation in temperature, catalyst concentration and MAO/catalyst molar ratio was also studied. Complex 5 ($R^1$: *n*-$C_4H_9$, $R^2$: H) showed a moderate conversion (37.4%) for the polymerization of methyl methacrylate. Copyright © 2005 John Wiley & Sons, Ltd.**

**KEYWORDS:** titanium; trityloxy; methylaluminoxane; olefin; polymerization

## INTRODUCTION

Following the discovery of the Ziegler–Natta catalyst used in the polymerization of ethylene,[1] olefin polymerization by organometallic catalysts has been a very active area of research. Research efforts have been devoted to understanding the way to control catalyst activity and selectivity, as well as the polymer composition and structure. To date, there have been many reports concerning this topic using metallocene catalysts, especially Group 4 metal complexes supported by the ubiquitous cyclopentadienyl (Cp) ligand because of interest from academic research and industry.[2–7] However, another branch of non-Cp complexes has also been extensively studied because of the easy access of ancillary ligands.[8,9] The diamido Group 4 metal complex reported by Scollard and McConville[10] was used in living polymerization of $\alpha$-olefins. More recently, Fujita and co-workers discovered that Group 4 metal complexes bearing the bidentate salicylaldimine or indolide-imine chelate ligands show extremely high activity toward ethylene polymerization.[11,12]

Therefore, interest in developing complexes with Cp and non-Cp mixed ligands has increased the potential for promising homogeneous catalysts for olefin polymerization.[13,14] We have reported a series of titanium(IV) complexes with mono-Cp and Schiff-base mixed ligands that show the advantages of Cp and non-Cp complexes in ethylene polymerization and ethylene–1-hexene copolymerization.[15] Recently, the $Cp'TiCl_2(OAr)$ or $Cp'TiCl_2[NAr(R)]$ complexes reported by Nomura and co-workers[16–18] have shown high catalytic activity in ethylene polymerization[16,17] and in ethylene–$\alpha$-olefin copolymerization[17,18]. These complexes, with a bulky ancillary ligand (OAr) or NAr(R) on the titanium center, were favorable for increasing the activity of $\alpha$-olefin polymerization.

Here, we report on the preparation of a series of new titanium(IV) complexes with mono-Cp and a monodentate bulky trityloxy group, and then focus on their catalytic behavior for the polymerization of $\alpha$-olefins in the presence of methylaluminoxane (MAO). The influence of different functional groups on the catalyst activity is also discussed.

## EXPERIMENTAL

All operations were carried out under a dry argon atmosphere using standard Schlenk techniques. Toluene, diethyl ether,

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Contract/grant sponsor: Major State Basic Research Projects; Contract/grant number: G1999064801.
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant number: 20072004.
Contract/grant sponsor: Research Fund for the Doctoral Program of High Education; Contract/grant number: 20020251002.

tetrahydrofuran (THF) and hexane were refluxed over sodium–benzophenone ketyl, from which they were distilled prior to use. Polymerization-grade ethylene was purified before use. $R^1CpTiCl_3$ was prepared by the reaction of $R^1CpSiMe_3$ with $TiCl_4$ in toluene.[19] $Ph_2(R^2C_6H_4)COH$ ($R^2C_6H_4$ = phenyl or *o*-methyl-phenyl) was synthesized by the reaction of $Ph_2CO$ with $R^2C_6H_4MgBr$ in diethyl ether.[20]

IR spectra were recorded on Nicolet Magna-IR 550 and Nicolet 5SXC spectrometers as KBr pellets. Elemental analyses were carried out on EA-1106 type analyzer. The $^1H$ NMR spectra were recorded on a Bruker AVANCE-500 MHz spectrometer with tetramethylsilane as internal standard and an HP 5989A instrument was used for mass spectrometry (MS).

## Synthesis of complexes 1–8 with the structure $R^1CpTiCl_2(OC(C_6H_4R^2)Ph_2)$

Complexes **1**–**8** were synthesized by a modified method according to literature.[21] The typical procedure was illustrated by the synthesis of **1**. Complexes **2**–**8** were synthesized by analogous procedures to complex **1**.

The complex $CpTiCl_3$ (1.251 g, 5.7 mmol) was dissolved in 100 ml diethyl ether to give a clear yellow solution. $Ph_3COH$ (1.485 g, 5.7 mmol) combined with $Et_3N$ (0.577 g, 5.7 mmol) in 40 ml diethyl ether was added dropwise over 1 h and stirred overnight. The mixture was filtered and recrystallized from toluene–hexane to give complex **1** in 78% yield. Analytical data for the $R^1CpTiCl_2(OC(C_6H_4R^2)Ph_2)$ complexes (**1**–**8**) are as follows.

Complex **1** ($R^1$: H; $R^2$: H): orange–yellow crystal, yield 78%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.41–7.27 (m, 15H, arom), 6.32 (s, 5H, $C_5H_5$). IR (KBr) $\nu$: 3109 (w), 3089 (w), 3059 (w), 3026 (w), 1597 (w), 1491 (m), 1445 (s), 1432 (w), 1319 (w), 1207 (w), 1081 (w), 1033 (s), 1017 (s), 1000 (s), 854 (m), 825 (s), 765 (m), 758 (s), 703 (s). MS (70 eV) $m/z$ (%): 372 (0.7, $[M - 2Cl]^+$), 243 (100), 65 (8, $Cp^+$). Anal. Found: C, 65.14; H, 4.66. Calc. for $C_{24}H_{20}Cl_2OTi$: C, 65.03; H, 4.56%.

Complex **2** ($R^1$: $CH_3$; $R^2$: H): orange crystal, yield 83%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.42–7.31 (m, 15H, arom), 6.13 (t, $J$ = 2.70 Hz, 2H, $C_5H_4$), 5.96 (t, $J$ = 2.70 Hz, 2H, $C_5H_4$), 2.33 (s, 3H, $CH_3$). IR (KBr) $\nu$: 3086 (w), 3059 (w), 3023 (w), 2924 (w), 1596 (w), 1492 (m), 1446 (m), 1375 (w), 1215 (w), 1155 (w), 1086 (w), 1044 (s), 1027 (s), 1001 (m), 900 (w), 826 (m). MS (70 eV) $m/z$ (%): 456 (0.3, $M^+$), 243 (100), 79 (3, $MeCp^+$); Anal. Found: C, 65.58; H, 5.07. Calc. for $C_{25}H_{22}Cl_2OTi$: C, 65.66; H, 4.86%.

Complex **3** ($R^1$: $PhCH_2$; $R^2$: H): orange–yellow crystal, yield 75%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.42–7.11 (m, 20H, arom), 6.15 (t, $J$ = 2.72 Hz, 2H, $C_5H_4$), 5.96 (t, $J$ = 2.72 Hz, 2H, $C_5H_4$), 4.05 (s, 2H, $CH_2Ph$). IR (KBr) $\nu$: 3103 (w), 3095 (w), 3084 (w), 3057 (w), 3027 (w), 2916 (w), 1594 (w), 1582 (w), 1487 (m), 1447 (m), 1440 (m), 1421 (w), 1316 (w), 1214 (w), 1155 (w), 1039 (s), 1032 (s), 1021 (s), 1000 (s), 745 (m), 707 (s), 630 (m). MS (70 eV) $m/z$ (%): 273 (100), 155 (37, $PhCH_2Cp^+$), 91 (15). Anal. Found: C, 69.97; H, 5.05. Calc. for $C_{31}H_{26}Cl_2OTi$: C, 69.80; H, 4.92%.

Complex **4** ($R^1$: cyclohexyl; $R^2$: H): orange–yellow crystal, yield 73%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.44–7.25 (m, 15H, arom), 6.22 (t, $J$ = 2.69 Hz, 2H, $C_5H_4$), 5.88 (t, $J$ = 2.69 Hz, 2H, $C_5H_4$), 2.88–2.80 (m, 1H, CH), 2.03–1.10 (m, 10H, $CH_2$). IR (KBr) $\nu$: 3424 (w), 3108 (w), 3096 (w), 3063 (w), 3033 (w), 2920 (s), 2849 (s), 1963 (w), 1596 (w), 1487 (s), 1446 (s), 1371 (m), 1322 (w), 1214 (m), 1155 (w), 1034 (s). MS (70 eV) $m/z$ (%): 377 (60.5, $[M - \textit{cyclo}\text{-}C_6H_{11}Cp]^+$), 265 (13.0, $[M - OPh_3]^+$), 243 (100), 147 (14.5, $\textit{cyclo}\text{-}C_6H_{11}Cp^+$). Anal. Found: C, 68.79; H, 5.85. Calc. for $C_{30}H_{30}Cl_2OTi$: C, 68.58; H, 5.77%.

Complex **5** ($R^1$: $n\text{-}C_4H_9$; $R^2$: H): yellow crystal, yield 72%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.43–7.26 (m, 15H, arom), 6.15 (t, $J$ = 2.69 Hz, 2H, $C_5H_4$), 5.95 (t, $J$ = 2.69 Hz, 2H, $C_5H_4$), 2.69 (t, $J$ = 7.83 Hz, 2H, $CH_2$), 1.54–1.46 (m, 2H, $CH_2$), 1.35–1.26 (m, 2H, $CH_2$), 0.89 (t, $J$ = 7.35 Hz, 3H, $CH_3$). IR (KBr) $\nu$: 3113 (w), 3098 (w), 3085 (w), 3064 (w), 3029 (w), 2942 (m), 2866 (m), 1594 (w), 1487 (s), 1447 (s), 1386 (m), 1317 (w), 1042 (s), 1024 (s), 902 (s), 834 (s). MS (70 eV) $m/z$ (%): 463 (2.5, $[M - Cl]^+$), 377 (4.3, $[M - {}^nBuCp]^+$), 243 (100), 239 (8.1, $[M - OPh_3]^+$), 121 (2.3, $^nBuCp^+$). Anal. Found: C, 67.41; H, 5.83. Calc. for $C_{28}H_{28}Cl_2OTi$: C, 67.34; H, 5.66%.

Complex **6** ($R^1$: $CH_2{=}CHCH_2$; $R^2$: H): deep-yellow crystal, yield 74%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.43–7.31 (m, 15H, arom), 6.21 (t, $J$ = 2.66 Hz, 2H, $C_5H_4$), 5.95 (t, $J$ = 2.66 Hz, 2H, $C_5H_4$), 5.94–5.85 (m, 1H, CH), 5.12–5.01 (m, 2H, $=CH_2$), 3.48 (d, $J$ = 6.65 Hz, 2H, $CH_2$). IR (KBr) $\nu$: 3104 (w), 3091 (m), 3057 (m), 3030 (w), 2970 (w), 1636 (w), 1595 (w), 1490 (s), 1442 (s), 1385 (w), 1207 (m), 1152 (w), 1036 (s), 1023 (s), 902 (s), 837 (s), 759 (s), 700 (s). MS (70 eV) $m/z$ (%): 412 (1.9, $[M - 2Cl]^+$), 243 (100), 223 (7.8, $[M - OPh_3]^+$), 105 (14.8, $CH_2{=}CHCH_2Cp^+$). Anal. Found: C, 67.21; H, 5.19. Calc. for $C_{27}H_{24}Cl_2OTi$: C, 67.09; H, 5.02%.

Complex **7** ($R^1$: $CH(CH_3)_2$; $R^2$: H): pale-yellow crystal, yield 72%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.45–7.27 (m, 15H, arom), 6.21 (t, $J$ = 2.69 Hz, 2H, $C_5H_4$), 5.83 (t, $J$ = 2.69 Hz, 2H, $C_5H_4$), 3.29–3.16 (m, 1H, CH), 1.20 (d, $J$ = 6.93 Hz, 6H, $CH_3$). IR (KBr) $\nu$: 3112 (w), 3089 (w), 3055 (w), 3031 (w), 2957 (m), 2928 (w), 2868 (w), 1599 (w), 1491 (m), 1461 (w), 1443 (s), 1420 (w), 1382 (w), 1206 (w), 1151 (w), 1011 (s), 998 (s), 837 (s), 759 (s), 699 (s). MS (70 eV) $m/z$ (%): 449 (1.8, $[M - Cl]^+$), 377 (1.6, $[M - {}^iPrCp]^+$), 243 (100), 107 (8.7, $^iPrCp^+$). Anal. Found: C, 67.06; H, 5.60. Calc. for $C_{27}H_{26}Cl_2OTi$: C, 66.81; H, 5.41%.

Complex **8** ($R^1$: H; $R^2$: $CH_3$): green–yellow crystal, yield 85%. $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$: 7.38–7.07 (m, 14H, arom), 6.33 (s, 5H, $C_5H_5$), 2.09 (s, 3H, $CH_3$). IR (KBr) $\nu$: 3120 (w), 3049 (w), 3036 (w), 2924 (w), 2854 (w), 1956 (w), 1656 (w), 1598 (w), 1491 (m), 1481 (m), 1444 (m), 1365 (w), 1286 (w), 1037 (s), 1018 (s), 1000 (s), 951 (m), 899 (m), 821 (s), 794 (m). MS (70 eV) $m/z$ (%): 257 (100), 65 (12, $Cp^+$). Anal. Found: C, 65.67; H, 4.91. Calc. for $C_{25}H_{22}Cl_2OTi$: C, 65.66; H, 4.86%.

## X-ray crystallography

The crystal data of complex **2** were collected on a Rigaku AFC-7R single crystal diffractometer at 293 K using Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å, graphite monochromatized, scan type $\omega-2\theta$). Intensities were corrected for Lorentz and polarization effects; an empirical psi-scans correction was applied (0.7521–1.0000). The structure was solved primarily by the direct methods using the SHELXS-97 system and refined by full-matrix least-squares on $F^2$ using all of the reflections with the SHELXL-97 program.

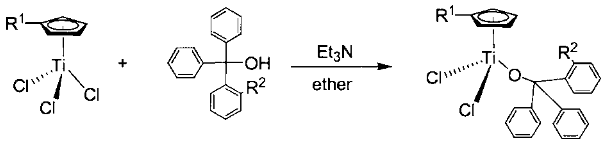
## Polymerization procedure

A proper flask was equipped with magnetic stirrer and vacuum line. The flask was filled with proper volume of freshly distilled toluene and monomer (ethylene, styrene or methyl methacrylate (MMA)). MAO was added, and the flask was placed in a bath at the desired temperature for 10 min. The polymerization reaction was started by adding a solution of the catalyst precursor with a syringe. The polymerization was carried out for the desired time and then quenched with 3% HCl in ethanol (200 ml). The precipitated polymer was filtered and then dried overnight in a vacuum oven at 60 °C.

# RESULTS AND DISCUSSION

## Synthesis and characterization

A general preparation route for the Cp and trityloxy mixed-ligand titanium complexes mentioned in this study is shown in Scheme 1. Considering the electronic and steric effects, a series of different substituents was chosen.[17,22] Complexes **1**–**8** could be readily synthesized in high yield in diethyl ether by the reaction of $R^1CpTiCl_3$ with $Ph_2(R^2C_6H_4)COH$ ($R^2C_6H_4$ = phenyl or *o*-methyl-phenyl) in the presence of $Et_3N$.



**1** $R^1$: H, $R^2$: H; **5** $R^1$: n-$C_4H_9$, $R^2$: H
**2** $R^1$: $CH_3$, $R^2$: H; **6** $R^1$: $CH_2{=}CHCH_2$, $R^2$: H
**3** $R^1$: $PhCH_2$, $R^2$: H; **7** $R^1$: $CH(CH_3)_2$, $R^2$: H
**4** $R^1$: cyclohexyl, $R^2$: H; **8** $R^1$: H, $R^2$: $CH_3$

**Scheme 1.**

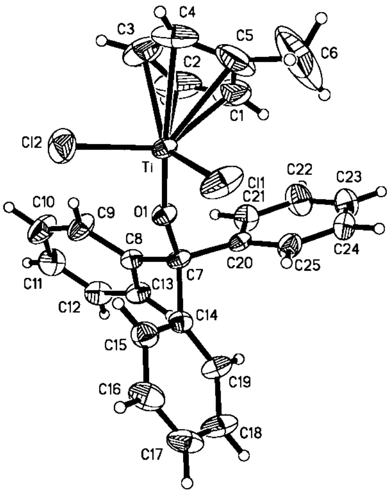


**Figure 1.** Crystal structure of $MeCpTiCl_2(OCPh_3)$ (**2**).

**Table 1.** Selected bond distances (Å) and bond angles (deg) for complex **2**

| | | | |
|---|---|---|---|
| Ti–O(1) | 1.7456(19) | Ti–C(2) | 2.292(4) |
| Ti–Cl(1) | 2.2334(11) | Ti–C(3) | 2.303(4) |
| Ti–Cl(2) | 2.2617(12) | Ti–C(5) | 2.371(5) |
| Ti–C(1) | 2.299(5) | O–C(7) | 1.426(3) |
| O(1)–Ti–Cl(1) | 101.73(8) | Cl(1)–Ti–C(2) | 138.3(2) |
| O(1)–Ti–Cl(2) | 102.50(8) | Cl(2)–Ti–C(2) | 113.3(2) |
| Cl(1)–Ti–Cl(2) | 101.34(6) | O(1)–Ti–C(1) | 96.79(18) |
| O(1)–Ti–C(2) | 93.02(16) | C(7)–O(1)–Ti | 164.5(2) |

An orange platelet microcrystal of **2** was grown from a toluene–hexane solution. The crystal structure is shown in Fig. 1, and selected bond distances and bond angles are presented in Table 1. The geometry around the titanium atom is tetrahedral and clearly shows piano-stool configuration. The Ti–O(1)–C(7) (alkoxy group) bond angle of complex **2** (164.5(2)°) is in the range of those complexes $Cp'TiCl_2(OAr)$ (162.3(2)–173.0(3)°) reported by Nomura *et al.*,[23] and the Ti–O(1) bond distance (1.7456(19) Å) is also quite close to the reported data of 1.760(4)–1.785(2) Å.[23]

## Polymerization of ethylene

The results of ethylene polymerization using complexes (**1**–**8**)/MAO are summarized in Table 2. All complexes showed higher catalytic activity than $CpTiCl_3$ except for complex **1**. Complex **2** showed the highest activity among them and exhibited a similar activity to that of $Cp_2TiCl_2$. A double bond (**6**) linked to the Cp ring led to an increase in the activity, probably due to its ability to stabilize the active metal center during the course of the polymerization, and the role of the double-bond functional group in catalyst activity was also recently studied by other researchers.[24,25]

The resultant polymer obtained by using **2** as the catalyst had the highest molecular weight ($M_\eta = 50.9 \times 10^4$) and was almost five times that of $Cp_2TiCl_2$ (catalyst **10**, $M_\eta = 10.2 \times 10^4$). The introduction of a illustrated by substituent on the Cp ring affects the molecular weight of the resultant polymer. This comparing entry 2 and entry 7 in Table 2, where we see that the isopropyl group in the Cp ring has decreased the molecular weight significantly, from $50.9 \times 10^4$ to $8.3 \times 10^4$, probably due to the steric effect imposed by the isopropyl group on the Cp ring.

**Table 2.** Ethylene polymerizarion catalyzed by complexes **1**–**8**/MAO[a]

| Entry | Catalyst | $x_{Al/Ti}$ | Yield (mg) | Activity × $10^{-4}$ ($g\ h^{-1}$ PE/mol Ti) | $M_\eta \times 10^{-4b}$ |
|---|---|---|---|---|---|
| 1 | **1** ($R^1$: H; $R^2$: H) | 1000 : 1 | 13.6 | 1.09 | n.d. |
| 2 | **2** ($R^1$: $CH_3$; $R^2$: H) | 1000 : 1 | 241.9 | 19.0 | $50.9 \times 10^4$ |
| 3 | **3** ($R^1$: $PhCH_2$; $R^2$: H) | 1000 : 1 | 51.5 | 4.12 | $21.1 \times 10^4$ |
| 4 | **4** ($R^1$: cyclohexyl; $R^2$: H) | 1000 : 1 | 79.4 | 6.35 | $11.0 \times 10^4$ |
| 5 | **5** ($R^1$: $n$-$C_4H_9$; $R^2$: H) | 1000 : 1 | 80.1 | 6.41 | $8.8 \times 10^4$ |
| 6 | **6** ($R^1$: $CH_2{=}CHCH_2$; $R^2$: H) | 1000 : 1 | 100.4 | 8.03 | $8.9 \times 10^4$ |
| 7 | **7** ($R^1$: $CH(CH_3)_2$; $R^2$: H) | 1000 : 1 | 122.5 | 9.80 | $8.3 \times 10^4$ |
| 8 | **8** ($R^1$: H; $R^2$: $CH_3$) | 1000 : 1 | 63.1 | 5.05 | $27.6 \times 10^4$ |
| 9 | **9** ($CpTiCl_3$) | 1000 : 1 | 26.1 | 2.09 | $33.9 \times 10^4$ |
| 10 | **10** ($Cp_2TiCl_2$) | 1000 : 1 | 591.3 | 47.3 | $10.2 \times 10^4$ |

[a] Conditions: $C_{Al} = 1.57\ mol\ l^{-1}$; cat.: 2.5 μmol; $T_p = 50\ °C$; solvent: toluene 25 ml; pressure: 1 atm; time: 0.5 h.
[b] Measured in decahydronaphthalene at 135 °C.

**Table 3.** Ethylene polymerizarion catalyzed by complex **2**/MAO under different aluminum/titanium molar ratios[a]

| Entry | $x_{Al/Ti}$ | Yield (mg) | Activity $\times 10^{-5}$ ($g\ h^{-1}$ PE/mol Ti) | $M_\eta \times 10^{-4b}$ |
|---|---|---|---|---|
| 11 | 500 : 1 | 152.7 | 1.22 | 62.7 |
| 2 | 1000 : 1 | 241.9 | 1.90 | 50.9 |
| 12 | 1500 : 1 | 250.3 | 2.00 | 10.0 |
| 13 | 2000 : 1 | 280.1 | 2.24 | 7.5 |

[a] Conditions: $C_{Al} = 1.57\ mol\ l^{-1}$; cat.: 2.5 μmol; $T_p = 50\ °C$; solvent: toluene 25 ml; pressure: 1 atm; time: 0.5 h.
[b] Measured in decahydronaphthalene at 135 °C.

As complex **2** was the most active one, the influence of the molar ratio of aluminum/titanium on the polymerization was studied, and the results are summarized in Table 3. It is obvious that a higher aluminum/titanium ratio is favorable for the polymerization of ethylene, but the molecular weight decreases at the same time.

In general, the higher the aluminum/titanium molar ratio, the higher the activity in ethylene polymerization. However, the catalytic activity showed a steep increase with the aluminum/titanium ratio from 500 to 1000 (entries 11 and 12), and then showed a very slow increase (entries 12 and 13). This implies that, for practical purposes, an aluminum/titanium ratio around 1000 is ideal for polymerization, as we an see from Table 3 that any further increase in aluminum/titanium molar ratio has little impact on activity. Such behavior is well explained by the influence of the aluminum concentration on the termination of polymer chains.[26] However, the molecular weight of the resultant polymer showed a great decrease when the aluminum/titanium ratio was increased from 1000 to 1500 (entries 2 and 12), whereas the catalytic activity showed just slight increase.

## Polymerization of styrene

The results of styrene polymerization using the **1**–**8**/MAO system are summarized in Table 4. This shows that a low concentration of titanium ($0.21\ mmol\ l^{-1}$) leads to higher activity and s-PS% in comparison with the polymerization condition using a doubled titanium concentration ($0.42\ mmol\ l^{-1}$), which is in agreement with the results reported by Ishihara *et al.*[27] The substituent on the Cp ring had a large influence on the activity and s-PS%, with complex **1** (entry 2) with a small steric group ($R^1$: H) on the Cp ring showing the highest activity ($1.45 \times 10^7\ g\ h^{-1}$ PS/(mol Ti)(mol S)) and s-PS% (98.3%). The benzyl group on the Cp ring (entry 6) decreased the activity ($1.77 \times 10^6\ g\ h^{-1}$ PS/(mol Ti)(mol S)) and s-PS% (78.3%) greatly due to the steric and electronic effects of the benzyl side chain, which may affect the active center during the polymerization procedure. Such behavior was also obtained by Rausch and co-workers[28] with the conclusion of the negative effect of the phenyl substituent in olefin polymerization. Comparing entry 2 and entry 12 in Table 4, we see that the alkenyl side chain on the Cp ring led to a large decrease in activity, but only had a slight effect on the s-PS% (91.2%) towards styrene polymerization.

The effects of temperature and time on the polymerization were studied further and the results are presented in Table 5 and Table 6 respectively for use of the **1**/MAO system. The data in Table 5 show that the activity increases as the temperature increases from 25 to 70 °C; the activity then decreases slightly when the temperature is increased further (Table 5, entry 21 and entry 22), together with a sharp decrease in the s-PS% from 97.5% to 75.5%. It was suggested that the active species formed by trityloxy derivatives are quite thermally stable for styrene polymerization under these conditions. However, as to the time of the polymerization, the highest activity was shown at the beginning of the polymerization (entry 23); a large decrease in activity was than observed, from $24.8 \times 10^6\ g\ h^{-1}$ PS/(mol Ti)(mol S) to

**Table 4.** Styrene polymerization catalyzed by complexes **1**–**8**/MAO[a]

| Entry | Catalyst | [Ti] (mmol $l^{-1}$) | Al/Ti | Activity × $10^{-6}$ (g $h^{-1}$ PS/(mol Ti)(mol S)) | s-PS[b] (%) |
|---|---|---|---|---|---|
| 1 | **1** ($R^1$: H; $R^2$: H) | 0.42 | 1000 : 1 | 12.5 | 97.3 |
| 2 | **1** ($R^1$: H; $R^2$: H) | 0.21 | 2000 : 1 | 14.5 | 98.3 |
| 3 | **2** ($R^1$: $CH_3$; $R^2$: H) | 0.42 | 1000 : 1 | 7.06 | 96.2 |
| 4 | **2** ($R^1$: $CH_3$; $R^2$: H) | 0.21 | 2000 : 1 | 7.83 | 97.6 |
| 5 | **3** ($R^1$: $PhCH_2$; $R^2$: H) | 0.42 | 1000 : 1 | 1.66 | 74.3 |
| 6 | **3** ($R^1$: $PhCH_2$; $R^2$: H) | 0.21 | 2000 : 1 | 1.77 | 78.3 |
| 7 | **4** ($R^1$: cyclohexyl; $R^2$: H) | 0.42 | 1000 : 1 | 3.78 | 90.0 |
| 8 | **4** ($R^1$: cyclohexyl; $R^2$: H) | 0.21 | 2000 : 1 | 5.20 | 91.3 |
| 9 | **5** ($R^1$: $n$-$C_4H_9$; $R^2$: H) | 0.42 | 1000 : 1 | 5.45 | 95.5 |
| 10 | **5** ($R^1$: $n$-$C_4H_9$; $R^2$: H) | 0.21 | 2000 : 1 | 6.96 | 97.0 |
| 11 | **6** ($R^1$: $CH_2{=}CHCH_2$; $R^2$: H) | 0.42 | 1000 : 1 | 2.52 | 90.3 |
| 12 | **6** ($R^1$: $CH_2{=}CHCH_2$; $R^2$: H) | 0.21 | 2000 : 1 | 4.23 | 91.2 |
| 13 | **7** ($R^1$: $CH(CH_3)_2$; $R^2$: H) | 0.42 | 1000 : 1 | 4.76 | 96.6 |
| 14 | **7** ($R^1$: $CH(CH_3)_2$; $R^2$: H) | 0.21 | 2000 : 1 | 6.80 | 97.7 |
| 15 | **8** ($R^1$: H; $R^2$: $CH_3$) | 0.42 | 1000 : 1 | 4.18 | 95.2 |
| 16 | **8** ($R^1$: H; $R^2$: $CH_3$) | 0.21 | 2000 : 1 | 6.10 | 96.3 |
| 17 | **9** ($CpTiCl_3$) | 0.42 | 1000 : 1 | 9.86 | 93.1 |
| 18 | **9** ($CpTiCl_3$) | 0.21 | 2000 : 1 | 12.1 | 91.9 |

[a] Conditions: $T_p = 50$ °C; $t_p = 1$ h; total volume: 12 ml; styrene concentration: 1.45 mol $l^{-1}$.
[b] Grams of 2-butanone insoluble polymer/grams of bulk polymer.

**Table 5.** Styrene polymerization catalyzed by complex **1**/MAO under different temperatures[a]

| Entry | Catalyst | $T_p$ (°C) | Al/Ti | Activity × $10^{-6}$ (g $h^{-1}$ PS/(mol Ti)(mol S)) | s-PS[b] (%) |
|---|---|---|---|---|---|
| 19 | **1** ($R^1$: H; $R^2$: H) | 25 | 2000 : 1 | 4.46 | 96.7 |
| 20 | **1** ($R^1$: H; $R^2$: H) | 50 | 2000 : 1 | 14.5 | 98.3 |
| 21 | **1** ($R^1$: H; $R^2$: H) | 70 | 2000 : 1 | 17.1 | 97.5 |
| 22 | **1** ($R^1$: H; $R^2$: H) | 90 | 2000 : 1 | 16.2 | 75.5 |

[a] Conditions: $t_p = 1$ h; total volume: 12 ml; [Ti] = 0.21 mmol $l^{-1}$; styrene concentration: 1.45 mol $l^{-1}$.
[b] Grams of 2-butanone insoluble polymer/grams of bulk polymer.

**Table 6.** Styrene polymerization catalyzed by complex **1**/MAO under different times[a]

| Entry | Catalyst | $t_p$ (h) | Al/Ti | Activity × $10^{-6}$ (g $h^{-1}$ PS/(mol Ti)(mol S)) | s-PS[b] (%) |
|---|---|---|---|---|---|
| 23 | **1** ($R^1$: H; $R^2$: H) | 1/6 | 2000 : 1 | 26.2 | 93.1 |
| 24 | **1** ($R^1$: H; $R^2$: H) | 0.5 | 2000 : 1 | 24.8 | 94.7 |
| 25 | **1** ($R^1$: H; $R^2$: H) | 1 | 2000 : 1 | 14.5 | 98.2 |
| 26 | **1** ($R^1$: H; $R^2$: H) | 1.5 | 2000 : 1 | 12.4 | 97.5 |
| 27 | **1** ($R^1$: H; $R^2$: H) | 2 | 2000 : 1 | 9.48 | 97.9 |

[a] Conditions: $T_p = 50$ °C; total volume: 12 ml; [Ti] = 0.21 mmol $l^{-1}$; styrene concentration: 1.45 mol $l^{-1}$.
[b] Grams of 2-butanone insoluble polymer/grams of bulk polymer.

$14.5 \times 10^6$ g $h^{-1}$ PS/(mol Ti)(mol S) (Table 5, entry 24 and entry 25), when the time was prolonged from 0.5 to 1 h. From Table 6 we could also see that the s-PS% of the resultant polymer was affected slightly by the polymerization time.

## Polymerization of MMA

In the light of the recently reported work by Chen and co-workers,[29] a half sandwich CGC–Ti complex showed high activity and stereo selectivity in MMA polymerization, which gave a high molecular weight and an extremely narrow polydispersity. Complexes were studied for MMA polymerization in the presence of MAO. It was found that only complex **5** with the *n*-butyl chain substituent on the Cp ring could initiate MMA polymerization (conversion 37.4%).

## CONCLUSIONS

A series of new titanium(IV) complexes with mono-Cp and monodentate bulky trityloxy mixed ligands was synthesized, and well characterized by $^1$H NMR, elemental analysis, IR spectroscopy and MS. A suitable crystal of complex **2** ($R^1$: $CH_3$; $R^2$: H) was obtained and the structure determined by X-ray diffraction. The title complexes were active for the polymerization of ethylene and styrene. Complex **2**, with a methyl substituent on the Cp ring, showed the same order of magnitude activity as that of $Cp_2TiCl_2$. For styrene polymerization, complex **1** ($R^1$: H; $R^2$: H) showed the highest activity ($1.45 \times 10^7$ g h$^{-1}$ PS/(mol Ti)(mol S)) and s-PS% (98.3%). Complex **5** ($R^1$: $n$-$C_4H_9$; $R^2$: H) was the only one able to initiate MMA polymerization (conversion 37.4%). From the above results of olefin polymerization, we observe that, in general, this series of new catalysts was effective at producing s-PS with high activity; however, there was low activity towards ethylene and MMA polymerization.

### Acknowledgements

This project was supported by the Special Funds for Major State Basic Research Projects (G1999064801), the National Natural Science Foundation of China (NNSFC) (20072004) and the Research Fund for the Doctoral Program of High Education (RFDP) (20020251002).

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