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Cyclopenta[l]phenanthrene titanium trichloride derivatives: syntheses, crystal structure and properties as catalysts for styrene polymerization

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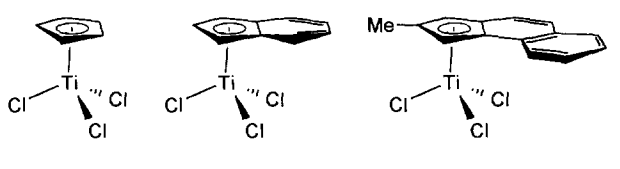
Abstract

Cyclopenta[l]phenanthrene titanium trichloride and its 2-methyl and phenyl derivatives were synthesized; the crystal structure of the 2-methyl-substituted complex was determined by X-ray diffraction analysis. In the presence of methylalumoxane (MAO), these complexes give highly active catalysts for the syndiotactic polymerization of styrene; the 2-phenyl-substituted complex exceeds all previously described catalysts in its catalytic activity. © 1997 Elsevier Science B.V.

1. Introduction

Since Ishihara and coworkers [1] discovered the syndiotactic polymerization of styrene with MAO-activated cyclopentadienyl titanium catalysts, the mechanism of the insertion reaction has been discussed controversially [2]. It seems to be established now that at temperatures above 0°C syndiotactic polystyrene (s-PS) is formed via a coordination-type Ziegler–Natta mechanism with a 15-electron Ti(III)-species being the active center [3]. This raises the question whether catalyst systems of this kind can be influenced in their properties by different cyclopentadienyl ligands in a manner similar to that observed in recent years for metallocene-based propene polymerization catalysts [4]. Recently, it has been shown that cyclopentadienyl systems with annelated six-rings (Fig. 1) are very active catalysts, which keep their productivity and syndiotacticity even at elevated temperatures [5,6]. In this paper we want to extend this correlation to three new catalysts **4**, **5** and **6**, which are derived from the cyclopenta[l]phenanthrene ligand system.



1 **2** **3**

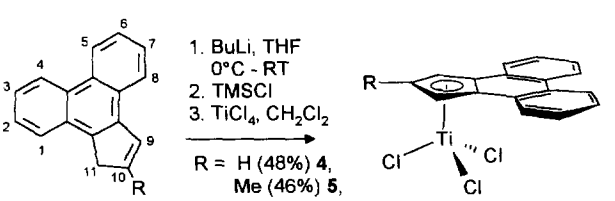
Fig. 1. Cyclopentadienyl titanium trichloride derivatives reported by Ishihara and coworkers (complex **1**) [1] and Rausch and coworkers (complexes **2** and **3**) [5,6] to catalyze the syndiospecific polymerization of styrene in the presence of MAO.

2. Results and discussion

Complexes **4**, **5** and **6** were synthesized from their precursors **7**, **8** and **9** [7] following procedures reported for related compounds (Fig. 2).

The structure of complex **5**, determined by an X-ray diffraction study (Fig. 3; Table 1), supports the close-to-tetrahedral geometry at the titanium center and the η^5-coordination of the annelated cyclopentadienyl ring.

Polymerizations were conducted by reacting styrene with complexes **4**, **5** and **6** in the presence of MAO at



7, 8, 9 **4, 5, 6**

Fig. 2. Syntheses of complexes **4–6**.

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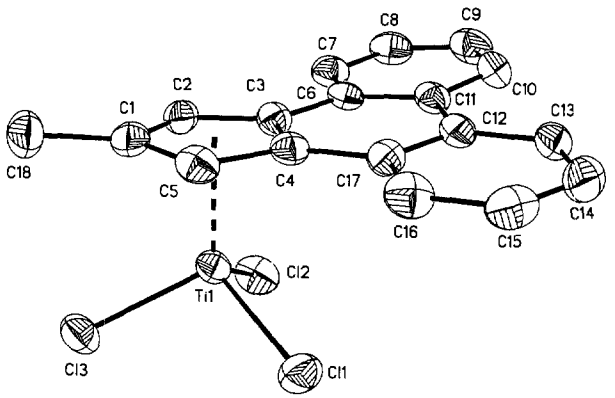

Fig. 3. Molecular structure of complex **5** (50% probability thermal elipsoids).

Table 1
Selected bond lengths (Å) and bond angles (°) for complex **5** with estimated standard deviations

Bond distances		Bond angles	
Ti(1)–Cl(1)	2.244(2)	Cl(1)–Ti(1)–Cl(2)	104.70(6)
Ti(1)–Cl(2)	2.235(2)	Cl(1)–Ti(1)–Cl(3)	102.01(5)
Ti(1)–Cl(3)	2.216(1)	Cl(2)–Ti(1)–Cl(3)	102.75(6)
Ti(1)–Centroid	2.041	C(18)–C(1)–Centroid	175.5
Ti(1)–C(1)	2.374(4)	Cl(1)–Ti(1)–Centroid	114.9
Ti(1)–C(2)	2.329(4)	Cl(2)–Ti(1)–Cenrtoid	114.8
Ti(1)–C(3)	2.400(4)	Cl(3)–Ti(1)–Centroid	116.0
Ti(1)–C(4)	2.409(4)		
Ti(1)–C(5)	2.344(4)		

different temperatures in toluene. For comparison, complex **3** (synthesized according to [6]) was also used as a polymerization catalyst under identical conditions [1]. All complexes except **4** exhibit their highest activities around 75°C. Above this temperature, deactivation seems to take place more readily [8]. The results (Table 2) show that complex **6** exhibits particularly high activities in the production of polystyrenes with high stereoregularity and molecular weight. This observation is probably due to the huge flat 'roof' over the active titanium tripod, which makes the titanium center sterically rather inaccessible; this steric congestion at the titanium center could possibly destabilize the formation of detrimental β-agostic interactions, which are thought to impede olefin insertions relative to chain termination by β–H-transfer. In addition, 'π-stacking' [9] between the aromatic ligand system and a coordinated styrene monomer might contribute to the high activity and stereospecificity.

3. Experimental section

All work involving air- or moisture-sensitive compounds was carried out using standard high-vacuum Schlenk or drybox techniques. Mass spectra were obtained using a Finnigan MAT 312 spectrometer. NMR spectra were recorded on Bruker AC 250 MHz, WM 250 MHz or DRX 600 MHz spectrometers (Internal standard $CDCl_3$: 7.24 ppm; C_6D_6: 7.16 ppm). The numbers in the NMR-data section refer to the labeling in Fig. 2.

Toluene and ether were distilled over Na, pentane over Na–K-alloy and CH_2Cl_2 over CaH_2 prior to use. Trimethylsilylchloride (Aldrich) was distilled over CaH_2. MAO was donated by Witco GmbH. 2,3-Dihydro-2-oxo-1H-cyclopenta[l]phenanthrene [10] was synthesized according to literature procedures. By reaction of the latter in a Shapiro-reaction or by addition of Methyl–Grignard reagent and subsequent dehydrogenation, 1H-cyclopenta[l]phenanthrene and 1H-2-methylcyclopenta[l]phenanthrene were obtained in 47% and 85% yield [7].

[1] For complex **3** we find activities which are considerably higher than those reported by Foster et al. under the same conditions [6]. This observation might have its reason in different grades of MAO used by them and by us.

Table 2
Polymerization of styrene with complexes **3–6** in the presence of MAO

Catalysator	50°C				75°C				100°C			
	A	SY	M_r	T_m	*A*	SY	M_r	T_m	*A*	SY	M_r	T_m
R = H (**4**)	4	64	6.9	246.4	7	49	4.2	241.0	41	88	1.9	n.d.
R = Me (**5**)	10	83	12.3	270.2	26	89	7.4	267.5	24	82	2.9	259.6
R = Ph (**6**)	40	85	27.7	267.8	75	92	13.0	265.2	45	90	5.8	264.9
(2-Me-benz[*e*]indene)$TiCl_3$ (**3**)[a]	15	88	14.8	270.3	76	89	9.3	267.8	42	92	7.1	267.6
	(18	93	42.4	275.2)	(15	91	18.8	261.0)	(7	90	10.6	258.4)

[Ti] = 50 μmol/l, Al:Ti = 4000:1, [styrene] = 0.88 M, reaction time: 10–20 min, activities *A* [$\times 10^7$ g PS/(mol Ti × mol styrene × h)], syndiotacticity SY (% insoluble in 2-butanone), molecular weight M_r ($\times 10^4$) determined by GPC, T_m (°C) determined by DSC.
[a] Data in parentheses from ref. [6] under identical conditions; molecular weights determined by intrinsic viscosity.

Differential scanning calorimetry (DSC) for melting transition (T_m) and gel permeation chromatography (GPC) for molecular weight determinations were recorded at BASF laboratories.

3.1. 1H-2-Phenyl-cyclopenta[l]phenanthrene (9)

2 ml (6 mmol) of a 3 M solution of phenylmagnesiumbromide in ether (Aldrich) were added dropwise at 0°C to 1.0 g 2,3-dihydro-2-oxo-1H-cyclopenta[l]phenanthrene (4.31 mmol) in 100 ml toluene. After warming to room temperature, the reaction mixture was stirred for 2 h and then hydrolyzed with 50 ml of a saturated aqueous solution of NH_4Cl and extracted with 300 ml of ether. The organic layers were extracted again with 100 ml of brine, dried over $MgSO_4$ and evaporated to dryness. The solid thus obtained was dissolved in 100 ml of toluene and stirred with 100 mg of *p*-toluene sulfonic acid under reflux for 2 h. After addition of 50 ml of a saturated aqueous solution of $NaHCO_3$ and extraction with 200 ml of ether, the organic layers were dried over $MgSO_4$ and evaporated to dryness. Flash-chromatography (pentane/ethyl acetate = 50:1) and subsequent evaporation in vacuo gave 2-phenyl-cyclopenta[l]phenanthrene as colorless needles. ^{1}H-NMR ($CDCl_3$; 600 MHz): δ 8.02 (d, $J = 7.7$ Hz, C_1-H), 7.62–7.56 (m, $C_{2,3}$-H), 8.68 (d, $J = 8.2$ Hz, C_4-H), 8.72 (d, $J = 7.1$ Hz, C_5-H), 7.66–7.64 (m, $C_{6,7}$-H), 8.20 (d, $J = 7.0$ Hz, C_8-H), 7.79 (s, C_9-H), 4.20 (s, 2 C_{11}-H), 7.75 (d, $J = 7.3$ Hz, 2 orthoPh-H), 7.42 (t, $J = 7.3$ Hz, 2 metaPh-H), 7.29 (t, $J = 7.3$ Hz, paraPh-H); assignments of the proton signals by DQF-COSY, ^{13}C, HMQC and ROESY measurements, MS (EI): m/z 292 (M^+, 100%), 215 (M^+-Ph, 6%), Anal. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.66; H, 5.63.

3.2. General method for the synthesis of 1-trimethylsilyl-cyclopenta[l]phenanthrene

To 10 mmol cyclopenta[l]phenanthrene, dissolved in 20 ml of THF and cooled with an icebath, 10 mmol of n-BuLi as a 1.6 M solution in hexane were added. The reaction mixture was stirred at room temperature overnight and the solvents removed under reduced pressure. After rinsing two times with 20 ml of pentane, the yellow to green residual solid was dissolved in 20 ml of THF and treated at room temperature with 12 mmol trimethylsilylchloride. The dark red solution was stirred again overnight, the solvent evaporated and the product extracted with 40 ml of pentane from which it was obtained by evaporation of the solvent.

3.3. 1-Trimethylsilyl-cyclopenta[l]phenanthrene

Yield: 90% (yellow oil). ^{1}H-NMR ($CDCl_3$; 250 MHz): δ 8.75–8.70 (m, 2 H), 8.26–8.22 (m, 1 H), 8.01–7.97 (m, 1 H), 7.65–7.53 (m, 4 H + 1 Cp-H), 6.89–6.86 (m, 1 CpH), 4.35 (bs, 1 Cp-H), −0.05 (s, 9 TMS-H), MS (EI): m/z 288 (M^+, 30%), 215 (M^+-TMS, 10%), 73 (TMS, 100%).

3.4. 1-Trimethylsilyl-2-methyl-cyclopenta[l]phenanthrene

Yield: 86% (yellow oil). ^{1}H-NMR ($CDCl_3$; 250 MHz): δ 8.71–8.64 (m, 2 H), 8.15–8.12 (m, 1 H), 7.88–7.85 (m, 1 H), 7.63–7.48 (m, 4 H), 7.13 (s, 1 CpH), 4.15 (s, 1 Cp-H), 2.35 (s, 3 Me-H), −0.08 (s, 9 TMS-H), MS (EI): m/z 302 (M^+, 40%), 228 (M^+-TMS, 10%), 73 (TMS, 100%).

3.5. 1-Trimethylsilyl-2-phenyl-cyclopenta[l]phenanthrene

Yield: 76% (beige solid). ^{1}H-NMR ($CDCl_3$; 250 MHz): δ 8.73–8.68 (m, 2 H), 8.27–8.24 (m, 1 H), 8.04–8.00 (m, 1 H), 7.68–7.53 (m, 4 H + 2 Ph-H), 7.70 (s, 1 CpH), 7.45–7.39 (m, 2 Ph-H), 7.32–7.25 (m, 1 Ph-H), 4.91 (s, 1 Cp-H), −0.30 (s, 9 TMS-H), MS (EI): m/z 364 (M^+, 20%), 291 (M^+-TMS, 7%), 73 (TMS, 65%).

3.6. General method for the synthesis of cyclopenta[l]phenanthrene titanium trichloride

1-Trimethylsilyl-cyclopenta[l]phenanthrene (amounts as obtained in the preceding reactions) was dissolved in 30 ml of CH_2Cl_2 and treated with the equimolar amount of titanium tetrachloride at 0°C. After stirring for 4 h at room temperature, the reaction mixture was concentrated to 15 ml in vacuo and cooled to −30°C overnight. Decantation of the mother liquor yielded the product as a red to purple solid.

3.7. Cyclopenta[l]phenanthrene titanium trichloride (3)

Yield: 53% red solid. ^{1}H-NMR ($CDCl_3$; 600 MHz): δ 8.56 (d, $J = 8.0$ Hz, $C_{4,5}$-H), 7.73–7.67 (m, $C_{2,3,6,7}$-H), 8.23 (d, $J = 7.4$ Hz, $C_{1,8}$-H), 7.62 (d, $J = 3.3$ Hz, $C_{9,11}$-H), 7.25 (t, $J = 3.3$ Hz, C_{10}-H), assignments of proton signals by ^{13}C and HMQC measurements, MS (EI): m/z 370 (M^+, 7%), 333 (M^+-Cl, 1%), 215 (7-H, 100%), Anal. Calcd for $C_{17}H_{11}TiCl_3$: C, 55.26; H, 3.00. Found: C, 54.77; H, 3.22.

3.8. 2-Methyl-cyclopenta-[l]-phenanthrene titanium trichloride (4)

Yield: 53% red needles. ^{1}H-NMR ($CDCl_3$; 600 MHz): δ 8.54 (d, $J = 7.9$ Hz, $C_{4,5}$-H), 7.71–7.65 (m, $C_{2,3,6,7}$-H), 8.18 (d, $J = 7.6$ Hz, $C_{1,8}$-H), 7.47 (s, $C_{9,11}$-H), 2.73 (s, Me-H), assignments of proton signals by

Table 3
Structure determination data for complex **5** ($C_{17}H_{11}Cl_3Ti$)

Space group	P-1	Diffractometer	Siemens P4
Crystal size (mm)	0.4 × 0.2 × 0.1	Radiation	MoK α
		T (K)	243
a (Å)	8.195(4)	Θ Limits (°)	2.06–25.05
b (Å)	9.849(3)	Scan mode	adaptive ω
c (Å)	10.022(3)	Reflections collected	3019
α (°)	83.60(1)	Obsd. reflections	2017
β (°)	81.91(3)	Parameters refined	251
γ (°)	87.98(2)	Weight scheme	$w^{-1} = \sigma^2 \times (F_0^2) + (0.0464P)^2 + 0.2744P$
V (Å^3)	795.7(5)	R	0.0477
Z	2	w$R2$	0.0983
D_c (g cm^{-3})	1.542	Residual density (eÅ^{-3})	+0.303/−0.320
μ (mm^{-1})	1.030		

During data collection three check reflections every 100 reflections were measured. The structure was solved by direct methods using the SHELX-86 program; for refinement the SHELX-93 program was used. All non-hydrogen atoms were refined anisotropic. Hydrogen atoms were taken from difference Fourier map and refined with fixed isotropic U.

^{13}C, and HMQC measurements, MS (EI): m/z 384 (M^+, 8%), 347 (M^+-Cl, 2%), 311 (M^+-2Cl, 2%), 229 (**8**-H, 100%), Anal. Calcd for $C_{18}H_{13}TiCl_3$: C, 56.37; H, 3.42. Found: C, 55.98; H, 3.54, X-ray structure data are given in Table 3; more information can be obtained at Fachinformationszentrum Karlsruhe, D-76344 Eggenstein–Leopoldshafen upon quotation of the depository number csb-406840, the authors and the journal reference of this article.

3.9. 2-Phenyl-cyclopenta[l]phenanthrene titanium trichloride (6)

Yield: 66% red solid. ^{1}H-NMR ($CDCl_3$; 600 MHz): δ 8.57 (d, $J = 7.7$ Hz, $C_{4,5}$-H), 7.74–7.69 (m, $C_{2,3,6,7}$-H), 8.29 (d, $J = 7.4$ Hz, $C_{1,8}$-H), 8.03 (s, $C_{9,11}$-H), 7.99 (d, $J = 7.4$ Hz, 2 *o*-Ph-H), 7.54 (t, $J = 7.4$ Hz, 2 *m*-Ph-H), 7.46 (t, $J = 7.4$ Hz, *p*-Ph-H), assignments of proton signals by ^{13}C, COSY and HMQC measurements, MS (EI): m/z 446 (M^+, 6%), 291 (**9**-H, 100%), Anal. Calcd for $C_{23}H_{15}TiCl_3$: C, 61.99; H, 3.39. Found: C, 61.67; H, 3.80.

3.10. Polymerization procedure for syndiotactic polystyrene

A 300-ml flask was charged with 50 ml of toluene, 5 ml (44 mmol) of freshly distilled styrene and 6 ml of MAO under an argon atmosphere. The flask was placed in an oil bath at the desired temperature and stirred for 10 min. The titanium catalyst (2.5 μmol, 1 ml of a 2.5 mM solution in toluene) was added via syringe and the reaction was stirred for 10 to 20 min. The reaction mixture was hydrolyzed by addition of 10% HCl in methanol, filtered, washed with excess methanol and dried over night at 100°C. The polymer was extracted with 2-butanone for 24 h in a Soxhlet extractor to remove atactic polymer and dried again at 100°C for 24 h.

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