Journal of Organometallic Chemistry, 381 (1990) 35–44
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20374

Synthetic, X-ray structural and polymerization studies on isopropyltetramethylcyclopentadienyl derivatives of titanium

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(Received May 3rd, 1989)

Abstract

The reaction of $TiCl_3(THF)_3$ with one equivalent of isopropyltetramethylcyclopentadienyllithium in THF followed by oxidation with HCl afforded $[\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4]TiCl_3$ (**1**) in 66% yield. Treatment of **1** with C_5H_5Tl in refluxing benzene gave $[\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4](\eta^5\text{-}C_5H_5)TiCl_2$ (**2**) in 95% yield. Reaction of $TiCl_3(THF)_3$ with two equivalents of isopropyltetramethylcyclopentadienyllithium in THF followed by oxidation with HCl afforded $[\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4]_2TiCl_2$ (**3**) in 73% yield. **3** crystallizes in the monoclinic space group $C2/c$ with a 17.032(2), b 8.275(2), c 19.078(4) Å, and β 120.83(1)° ($Z = 4$). Least-squares refinement leads to a final R (based on F) of 0.038 for 2658 independent reflections. The structure consists of a bent sandwich structure with a CNT–Ti–CNT (CNT = ring centroid) angle of 137.4(1)° and an unusually acute Cl–Ti–Cl bond angle of 88.81(4)°. Ethylene polymerizations by $[\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4](\eta^5\text{-}C_5H_5)TiCl_2$/MAO (MAO = methylalumoxane), $[\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4]_2TiCl_2$/MAO, and $(\eta^5\text{-}C_5H_5)_2TiCl_2$/MAO are compared at 1.3 atm over the temperature range of 0–50 °C.

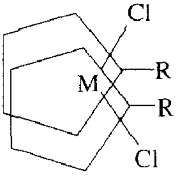
Introduction

It has been well established that replacement of an η^5-cyclopentadienyl ligand by an η^5-pentamethylcyclopentadienyl ligand in transition metal complexes results in significant changes in reactivity, stability, and other properties, owing to both the steric and electronic changes that accompany replacement of the hydrogen atoms by

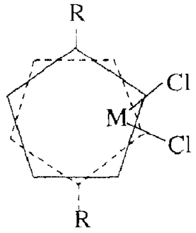
0022-328X/90/$03.50

methyl substituents. The pentamethylcyclopentadienyl ligand has been widely utilized in organometallic chemistry because of this electron donating ability and steric bulk. However, considerably less work has been focused on ligands in which one of the methyl groups has been replaced by a more bulky substituent [1,2].

The molecular geometries of the bis(η^5-alkylcyclopentadienyl)metal dihalides, which have been structurally characterized, have been found to be dictated primarily by the steric requirements of the alkyl substituent [3,4]. The ring orientation in the bis(η^5-alkylcyclopentadienyl)titanium dihalide derivatives that have been structurally characterized to date can be divided into two categories which are illustrated schematically by I and II. In $(CH_3C_5H_4)_2TiCl_2$ and $[(CH_3)_2CHC_5H_4]_2TiCl_2$ the substituted cyclopentadienyl rings were found to be as in I [3d,e]. However, with the more bulky t-butyl groups in $[(CH_3)_3CC_5H_4]_2TiCl_2$ the cyclopentadienyl rings adopt an orientation represented by II [3a]. In $(\eta^5\text{-}C_5H_5)_2TiCl_2$, $(\eta^5\text{-}C_5(CH_3)_5)_2TiCl_2$ and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5(CH_3)_5)TiCl_2$ the cyclopentadienyl rings have been found to be staggered [3b,c,i].



I



II

Recent studies in our laboratories have been directed toward the synthesis and structural comparisons of Group IV metallocene derivatives. One of us has recently shown that the addition of nucleophiles to 1,2,3,4,6-pentamethylfulvene is a convenient route for the preparation of substituted tetramethylcyclopentadienyl anions such as isopropyltetramethylcyclopentadienyllithium [2]. We report here the synthesis, X-ray structure, and polymerization studies on isopropyltetramethylcyclopentadienyl derivatives of titanium.

Experimental

All operations were carried out under an argon atmosphere using standard Schlenk, vacuum, or dry box techniques. Argon was deoxygenated with BTS catalyst and dried with molecular sieves and P_2O_5. Diethyl ether and tetrahydrofuran (THF) were predried over sodium wire and distilled under argon from sodium/potassium alloy. Hexane and benzene were dried and distilled under argon over sodium/potassium alloy, while dichloromethane was distilled from calcium hydride under argon. Aldrich HPLC grade toluene was stirred over H_2SO_4 for 2 weeks, neutralized with Na_2CO_3, washed with H_2O, dried over $MgSO_4$, and distilled from Na under argon, then distilled under argon from CaH_2 prior to use as solvent in polymerizations studies. Cyclopentadienylthallium was prepared as described by Hunt and Doyle [5], titanium trichloride tris(tetrahydrofuran) was prepared as described by Manzer [6], isopropyltetramethylcyclopentadienyllithium was prepared by the method of Bensley and Mintz [2a], and methylalumoxane (MAO) was prepared as previously reported [7]. Microanalyses were performed by the Microanalytical

Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using a Varian Associates XL-200 NMR spectrometer with tetramethylsilane (TMS) as an internal standard.

Trichloro-(η^5-isopropyltetramethylcyclopentadienyl)titanium (1). Trichlorotris(tetrahydrofuran)titanium, $[TiCl_3(THF)_3]$, (2.39 g, 6.45 mmol) and isopropyltetramethylcyclopentadienyllithium (1.10 g, 6.45 mmol) were weighed into a 50 ml Schlenk flask. Dry THF (30 ml) was added and the mixture was stirred at room temperature for 18 h. The reaction mixture was then cooled to 0 °C and dry HCl was bubbled through the solution for 5–10 min. After stirring for an additional hour at room temperature, the solvent was removed under vacuum and the resulting red residue extracted with benzene and filtered through celite. The benzene was removed under vacuum and the residue was washed with cold pentane, dried, and sublimed at 140–150 °C/10^{-3} torr, yielding 1.35 g (66%) of **1** as a bright red solid. NMR data in Tables 4 and 5. EI mass spectrum [8*], m/z 316 $(M)^+$, 281 $(M-Cl)^+$, 246 $(M-2Cl)^+$, 163 $(Cp^\star)^+$. ($Cp^\star$ = i-$PrMe_4C_5$) (Found: C, 45.66; H, 6.31. $C_{12}H_{19}Cl_3Ti$ calcd.: C, 45.39; H, 6.03%).

Dichloro(η^5-cyclopentadienyl)(η^5-isopropyltetramethylcyclopentadienyl)titanium (2). Trichloro(η^5-isopropyltetramethylcyclopentadienyl)titanium (**1**) (0.72 g, 2.3 mmol) and cyclopentadienylthallium (0.61 g, 2.3 mmol) were weighed into a 50 ml Schlenk flask and approximately 20 ml of dry benzene was added. A condenser was attached and the mixture was refluxed for 18 h. The reaction mixture was cooled to room temperature and filtered through celite to remove thallium chloride. Removal of the benzene under vacuum yielded 0.75 g (95%) of **2** as violet crystals. An analytically pure sample was obtained by recrystallization of the product from CH_2Cl_2/hexane. NMR data in Tables 4 and 5. EI mass spectrum [8*], m/z 346 $(M)^+$, 311 $(M-Cl)^+$, 281 $(M-Cp^\star)^+$, 163 $(Cp^\star)^+$. (Found: C, 58.62; H, 7.05. $C_{17}H_{24}Cl_2Ti$ calcd.: C, 58.81; H, 6.97%).

Dichlorobis(η^5-isopropyltetramethylcyclopentadienyl)titanium (3). Dichlorobis(η^5-isopropyltetramethylcyclopentadienyl)titanium was prepared in a manner similar to **1** except that 0.92 g (5.4 mmol) of isopropyltetramethylcyclopentadienyllithium and 1.0 g (2.7 mmol) of $TiCl_3(THF)_3$ were used. After removal of the solvent under vacuum the residue was dissolved in CH_2Cl_2, filtered through celite, and the solution concentrated under vacuum. Hexane was added and the solution cooled to −20 °C to yield 0.44 g (73%) of **3** as purple crystals. NMR data are given in Tables 4 and 5. EI mass spectrum [8*], m/z 444 $(M)^+$, 409 $(M-Cl)^+$, 281 $(M-Cp^\star)^+$, 163 $(Cp^\star)^+$. (Found: C, 64.80; H, 8.75. $C_{24}H_{38}Cl_2Ti$ calcd.: C, 64.72; H, 8.60%).

Polymerization studies. Ethylene polymerizations were carried out in 250 ml pressure bottles using magnetic stirring and using toluene as the solvent. Toluene (90 ml) was introduced into a metal crimp-capped crown bottle fitted with butyl rubber liners under an atmosphere of argon. MAO (0.250 g in 10 ml of toluene) and the appropriate metallocene (2.0×10^{-6} mol) were injected into the reactor. The polymerizations were performed at 0, 25, and 50 °C for 2 h under 20 psig of ethylene [9]. At the end of this time acidic methanol was added to the system to

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Crystallographic data for $C_{24}H_{38}Cl_2Ti$

(a) Crystal parameters			
formula	$C_{24}H_{38}Cl_2Ti$	Z	4
crystal system	monoclinic	D(calcd), g cm^{-3}	1.280
space group	$C2/c$	T, K	293
a, Å	17.032(2)	size	0.23 × 0.29 × 0.34
b, Å	8.275(2)	color	red
c, Å	19.078(4)	μ(Mo-K_α), cm^{-1}	6.19
β, deg	120.83(1)	T_{max}/T_{min}	0.856/0.781
V, Å^3	2311.2(8)		
(b) Data collection			
diffractometer	Nicolet R3m/μ	rflns collected	2922
radiation	Mo-K_α	indpdt rflns	2658
wavelength, Å	0.71073	R(merge), %	1.2
monochromator	graphite	obs rflns ($3\sigma F_o$)	2115
scan limits, deg	$4 \leq 2\theta \leq 55$	std rflns	3 std/197 rflns
scan method	Wyckoff	decay, %	< 1
(c) Refinement			
$R(F)$, %	3.81	Δ/σ(mean)	0.028
$R(wF)$, %	4.21	$\Delta(\rho)$, e Å^{-3}	0.23
GOF	1.200	N_o/N_v	10.6

quench the polymerization. The polymer was filtered, washed with methanol and dried under vacuum. See Table 7.

Crystal structure determination. Crystallographic data are collected in Table 1. Crystals were mounted in epoxy cement and photographically determined to be of monoclinic symmetry. Systematic absences in the diffraction data indicated either of the space groups $C2/c$ or Cc. The former, centrosymmetric, choice was confirmed

Table 2

Atomic coordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^3) for $C_{24}H_{38}Cl_2Ti$

	x	y	z	U[a]
Ti	5000	994.1(5)	7500	26.7(2)
Cl	4449.6(4)	3034.5(6)	6490.5(3)	44.1(3)
C(1)	3384(1)	299(2)	6742(1)	31.5(8)
C(2)	3509(1)	1406(3)	7361(1)	34.4(9)
C(3)	4057(2)	648(3)	8128(1)	36.6(9)
C(4)	4289(1)	−912(3)	7994(1)	34.7(8)
C(5)	3856(1)	−1149(2)	7132(1)	33.3(8)
C(6)	2721(2)	589(3)	5845(1)	38.6(9)
C(7)	3009(2)	−5(3)	5253(2)	53(1)
C(8)	1784(2)	−141(4)	5613(2)	58(1)
C(9)	3085(2)	3040(3)	7252(2)	47(1)
C(10)	4233(2)	1270(3)	8931(1)	54(1)
C(11)	4666(2)	−2206(3)	8634(2)	50(1)
C(12)	3711(2)	−2789(3)	6752(2)	46(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected bond distances and angles for $C_{24}H_{38}Cl_2Ti$

(a) Bond distances (Å)			
Ti–CNT [a]	2.130(2)	Ti–C(5)	2.456(2)
Ti–Cl	2.364(1)	C(1)–C(2)	1.422(3)
Ti–C(1)	2.432(2)	C(2)–C(3)	1.417(3)
Ti–C(2)	2.438(3)	C(3)–C(4)	1.412(3)
Ti–C(3)	2.465(3)	C(4)–C(5)	1.428(3)
Ti–C(4)	2.452(3)	C(5)–C(1)	1.422(3)
(b) Bond angles (deg)			
CNT–Ti–CNT [a]	137.4(1)	CNT–Ti–Cl	105.3(1)
Cl–Ti–Cl [a]	88.81(4)	CNT–Ti–Cl_a	104.8(1)

[a] CNT = centroid of C(1) to C(5).

Table 4

^1H NMR data for new $Cp^{\star}$ titanium derivatives [a,b]

Compound	Cp	$C_5(CH_3)_4$	CH_3	CH
$Cp^{\star}TiCl_3$		2.32 (s) 6H 2.48 (s) 6H	1.32 (d) 6H	3.42 (sep) 1H
$Cp^{\star}CpTiCl_2$	6.35 (s) 5H	2.00 (s) 6H 2.25 (s) 6H	1.12 (d) 6H	3.10 (sep) 1H
$Cp^{\star}_2TiCl_2$		2.00 (s) 12H 2.15 (s) 12H	1.10 (d) 12H	3.20 (sep) 2H

[a] Chemical shifts δ in ppm relative to internal TMS in $CDCl_3$ at 25 °C; (multiplicity) [s = singlet; d = doublet; sep = septet]; intensity. [b] $Cp^{\star} = [\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4]$.

by the presence of a two-fold molecular symmetry and a centrosymmetric lattice. The data were empirically corrected for absorption.

The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were found and isotropically refined. All computations used SHELXTL (5.1) software (G.

Table 5

$\{^1H\}^{13}C$ NMR data for new $Cp^{\star}$ titanium derivatives [a,b]

Compound	Cp	$C_5(CH_3)_4$	$C_5(CH_3)_4$	$(CH_3)_2$	CH
$Cp^{\star}TiCl_3$		14.4 15.1	136.3 138.8 148.2	21.9	30.1
$Cp^{\star}CpTiCl_2$	120.0	13.5 14.1	130.4 130.8 137.5	21.5	29.0
$Cp^{\star}_2TiCl_2$		12.9 13.7	127.1 128.5 140.3	21.4	28.9

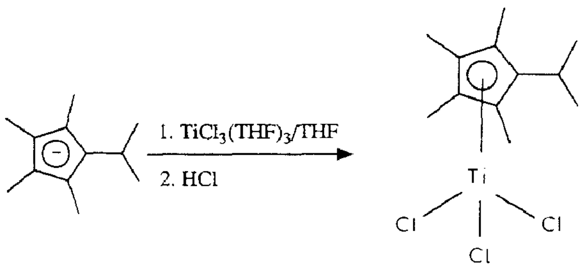
[a] Chemical shifts δ in ppm relative to internal TMS in $CDCl_3$ at 25 °C. [b] $Cp^{\star} = [\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4]$.

Sheldrick, Nicolet XDR, Madison, WI). Atomic coordinates are given in Table 2 and selected bond distances and angles in Table 3.

Results and discussion

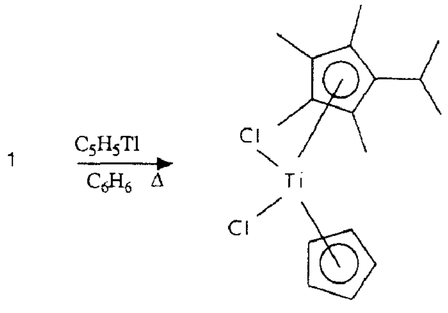
Syntheses. Isopropyltetramethylcyclopentadienyllithium was prepared by treatment of 1,2,3,4,6-pentamethylfulvene with methyllithium [2]. The starting material 1,2,3,4,6-pentamethylfulvene was prepared by the addition of vinylmagnesium bromide to 2,3,4,5-tetramethylcyclopent-2-enone [2].

A reaction of isopropyltetramethylcyclopentadienyllithium with one equivalent of $TiCl_3(THF)_3$ in THF followed by oxidation with HCl and removal of the solvent gave a red residue. Extraction with benzene, filtration through celite, removal of the solvent and sublimation of the residue afforded trichloro(η^5-isopropyltetramethylcyclopentadienyl)titanium, $[\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4]TiCl_3$ (**1**) in 66% yield as a bright red solid. Complex **1** was characterized by elemental analysis and by its ^1H and ^{13}C NMR spectra (Tables 4 and 5).



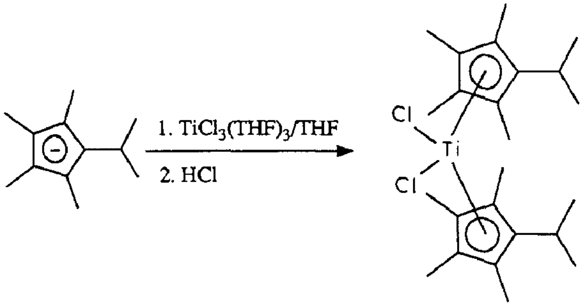
1

By adaptation of the procedure of Rausch and co-workers [3i] for the synthesis of $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)TiCl_2$, we have synthesized $[\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4](\eta^5\text{-}C_5H_5)TiCl_2$ (**2**). Thus, a reaction between $[\eta^5\text{-}(CH_3)_2CHC_5Me_4]TiCl_3$ (**1**) and C_5H_5Tl in refluxing benzene produced, after work-up, **2** in 95% yield. Complex **2** was obtained as fine violet crystals and was characterized by elemental analysis and its ^1H and ^{13}C NMR spectra (Tables 4 and 5).



2

The reaction of $[TiCl_3(THF)_3]$ with two equivalents of isopropyltetramethylcyclopentadienyllithium in THF followed by oxidation with HCl and removal of the solvent produced a red residue. This red residue was extracted with CH_2Cl_2, filtered through celite, and the solvent concentrated under vacuum. Addition of hexane and cooling to −20 °C gave **3** as purple crystals in 73% yield. Complex **3** was characterized by elemental analysis and by its ^1H and ^{13}C NMR spectra, Tables 4 and 5.



3

Structure of $(\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4)_2TiCl_2$ *(3)*

An ORTEP illustration of the molecular structure and atom labelling scheme for **3** is given in Fig. 1. Selected bond distances and angles can be found in Table 3. The geometry at titanium is pseudotetrahedral. The centroids of the two π-bonded rings and the two chlorine atoms make the four vertices. The ring centroid-titanium-ring centroid angle of 137.4(1)° in **3** is identical, within experimental error, to that in $(\eta^5\text{-}C_5(CH_3)_5)_2TiCl_2$ [3c]. However, the Cl–Ti–Cl bond angle at 88.81(4)° is unusually acute (see Table 6). Another unusual feature of this structure is that the cyclopentadienyl rings are only partially staggered, with an average relative displacement of 16.2° (Fig. 2), compared with 36° required for a "perfect" staggered conformation. The isopropyl groups in **3** are located at opposite sides of the molecule, directed away from each other and the chlorine atoms, with one of the methyl groups of each isopropyl group directed towards the titanium atom and one

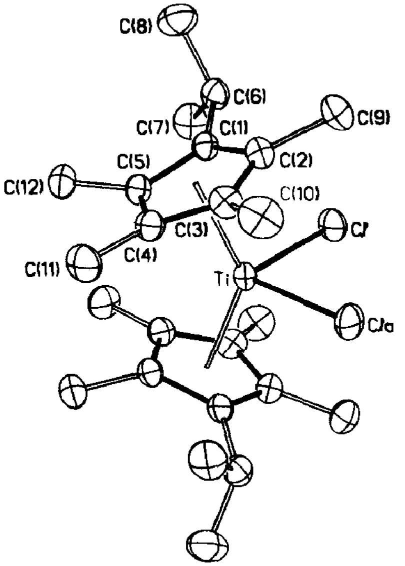


Fig. 1. Molecular structure and atom labelling scheme for **3**. The atoms are represented by their 40% probability ellipsoids for thermal motion. Hydrogen atoms are omitted for clarity.

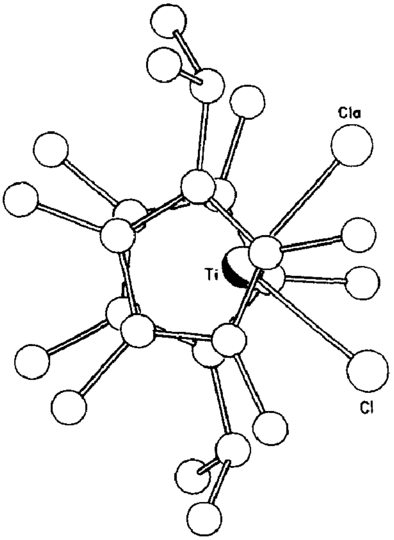


Fig. 2. View of **3** illustrating the relative conformation of the Cp* ligands.

Table 6

Structural parameters for some η^5-Cp_2TiCl_2 complexes

	Structure type	Cp–M–Cp (°)	Cl–M–Cl (°)	Reference
$(\eta^5\text{-}C_5H_5)_2TiCl_2$	Staggered	131.0(av.)	94.5(av.)	3b
$(\eta^5\text{-}C_5(CH_3)_5)_2TiCl_2$	Staggered	137.4	92.94(4)	3c
$(\eta^5\text{-}(CH_3)C_5H_4)_2TiCl_2$	I	130.2	93.15(8)	3d
$(\eta^5\text{-}(CH_3)_2CHC_5H_4)_2TiCl_2$	I	132.9	92.5(1)	3e
$(\eta^5\text{-}(CH_3)_3CC_5H_4)_2TiCl_2$	II	131.5	92.5(5)	3a
$(\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4)_2TiCl_2$		137.4	88.81(4)	this work

Table 7

Ethylene polymerization activities for Cp_2TiCl_2, $Cp^*CpTiCl_2$, and $Cp^*_2TiCl_2$-MAO catalysts [a]

Metallocene	Yield [b] (activity) [c] (at 0 °C)	Yield [b] (activity) [c] (at 25 °C)	Yield [b] (activity) [c] (at 50 °)
Cp_2TiCl_2	1.20 [d]	1.23	0.23
	(432)	(220)	(41.0)
$Cp^*CpTiCl_2$	0.15	0.74	0.060
	(27.0)	(130)	(11.0)
$Cp^*_2TiCl_2$	(1.03)	0.08	0.004
	(5.0)	(14)	(0.7)

[a] Metallocene 2.0×10^{-6} mol; 0.250 g MAO; 100 ml toluene; $P(C_2H_4)$ 1.3 atm; 2 h; $Cp^* = [\eta^5\text{-}(CH_3)_2CHC_5(CH_3)_4]$. [b] g polyethylene. [c] (kg polyethylene)/(mol catalyst)(atm C_2H_4)(h). [d] Polymerization carried out for 1 h only (ref. 9).

methyl group directed away from the titanium. In contrast, the isopropyl groups in $(\eta^5\text{-}(CH_3)_2CHC_5H_4)_2TiCl_2$ are located directly above and below the $TiCl_2$ group and both of the methyl groups of the isopropyl group are directed away from the titanium atom [3e].

Ethylene polymerization studies

A major advance in α-olefin polymerization occurred when Kaminsky and coworkers discovered that a combination of $(\eta^5\text{-}C_5H_5)_2MCl_2$ (M = Ti, Zr) and oligomeric methylalumoxanes (MAO) produced an exceedingly active Ziegler–Natta polymerization catalyst [10]. We have examined the activity of **2**/MAO and **3**/MAO as catalysts for the polymerization of ethylene and compared them with $(\eta^5\text{-}C_5H_5)_2TiCl_2$/MAO at 0, 25, and 50 °C (Table 7). Chien [11] has previously shown that Ziegler–Natta polymerization catalysts prepared from Cp_2TiCl_2 and organoaluminum halides suffer from rapid deactivation by bimolecular reductive disproportionation. We hoped that by utilizing titanocene derivatives containing bulky cyclopentadienyl ligands, that we could prepare longer lived olefin polymerization catalysts. However, the data in Table 7 indicate that as the steric bulk around the titanium metallocene increases in these systems, the activity of the catalyst formed upon treatment of the metallocene dichloride with MAO decreases. Similar reactivity trends involving substituted zirconocene dichloride/MAO catalysts have been observed by Kaminsky and coworkers [12]. The dramatic loss in polymerization activity upon heating these catalyst systems to 50 °C suggests that increasing the steric bulk about the titanium atom is not sufficient to overcome deactivation, at least in these systems [13*].

Supplementary material available. Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (4 pages) and a listing of observed and calculated structure factors (13 pages) are available from A.L. Rheingold.

Acknowledgment

We are grateful to Fina Oil and Chemical Company (MDR), and to the Donors to the Petroleum Research Fund, administered by the American Chemical Society (MDR), for support of this research program. We also wish to thank Prof. Helmut Alt for assistance in obtaining the mass spectra.

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