

SYNTHESIS OF TRICHLORO(η^5 -ALKENYLTETRAMETHYL-CYCLOPENTADIENYL)TITANIUM(IV) COMPLEXES AND THEIR ACTIVITY IN STYRENE POLYMERIZATION

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Received June 11, 2001
Accepted August 1, 2001

Fully substituted trichloro(η^5 -cyclopentadienyl)titanium(IV) complexes with pendant alkenyl groups, $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]$ (R = CH(Me)CH=CH₂ (**3a**), (CH₂)₂CH=CH₂ (**3b**), and (CH₂)₃CH=CH₂ (**3c**)), were synthesized by the reaction of the corresponding trimethylsilyl or trimethylstannyl substituted cyclopentadienes C₅Me₄R(EMe₃), where E = Si or Sn, with TiCl₄. In all cases, the pendant double bonds did not exhibit any interaction with the titanium atoms as indicated by ¹H, ¹³C NMR or IR spectra as well as by the solid-state structure of **3c**. The catalytic systems prepared by mixing complexes **3a–3c**, $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]$, $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]$, and similar complexes with R = butyl (**4**), phenyl (**5**), 4-fluorophenyl (**6**) with methylalumoxane (MAO) at the molar ratio Al/Ti = 500 catalyzed polymerization of styrene to syndiotactic polystyrene. Their polymerization activities increase in the order: $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)] < \mathbf{3a} < \mathbf{3b} < \mathbf{3c} < \mathbf{4} < \mathbf{5} < \mathbf{6} < [\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]$, while the molecular weights (M_w) of syndiotactic polystyrene grow in the order: $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)] < \mathbf{3a} < \mathbf{3b} < \mathbf{4} \approx \mathbf{6} < [\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)] < \mathbf{3c} \approx \mathbf{5}$ (maximum M_w ca 3.0 · 10⁵). A comparison of the results for the catalytic systems based on **4** with those derived from **3a–3c** points to a rather weak competition of the pendant double bonds with monomer for a cationic Ti(III) catalytic centre.

Keywords: Titanium; Half-sandwich complexes; Trichloro(cyclopentadienyl)titanium complexes; Substituted cyclopentadienyl ligands; Pendant alkenyl groups; Crystal structure; Styrene; Cationic polymerizations; Syndiotactic polystyrene.

Derivatives of group 4 metallocene dichlorides bearing substituents with a pendant double bond attract attention as potential precursors of cationic

catalysts for polymerization of alkenes¹⁻³. Pendant double bonds can be used for anchoring the metallocene dichlorides onto silica supports through catalytic hydrosilylation with $\text{SiMe}_2(\text{H})\text{Cl}$ followed by a reaction of the SiMe_2Cl -functionalized metallocenes with surface Si-OH groups⁴. Alternatively, the complexes themselves combined with methylalumoxane (MAO) can copolymerize with alkenes to give polymer-bound catalysts, whose efficiency (the molecular weight of the polymer in particular) is influenced by the length of the alkenyl chain^{5,6}. In this regard, trichloro(η^5 -cyclopentadienyl)titanium(IV) complexes containing alkenyl groups with terminal double bonds on the η^5 -cyclopentadienyl ligand combined with methylaluminoxane (MAO) offer another possibility to demonstrate the effect of alkenyl chain length on the polymer chain transfer in the polymerization of styrene or ethene. Investigation into this field is of interest since recent comparative studies of styrene polymerization using catalysts based on 1-substituted trichloro(η^5 -indenyl)titanium(IV)^{7a,7b} and trichloro(η^5 -1,2,3,4,-tetramethyl-5-phenethylcyclopentadienyl)trichlorotitanium(IV)^{7c} complexes do not provide a plausible account for the observed results.

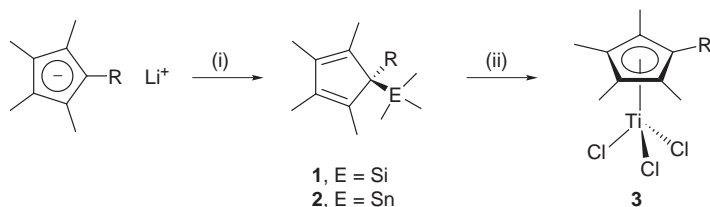
Here we report the synthesis of a series of complexes $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]$ [$\text{R} = \text{CH}(\text{Me})\text{CH}=\text{CH}_2$ (**3a**), $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (**3b**), $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (**3c**), butyl (**4**), phenyl (**5**), and 4-fluorophenyl (**6**)] and their use as catalyst components for styrene polymerization in combination with MAO co-catalyst. The study is aimed at establishing the effect of pendant alkenyl groups on the molecular weight of polymer and polymerization activity in comparison with effects of some conventional substituents R.

RESULTS AND DISCUSSION

Synthesis of Catalysts

Synthesis of trichloro(η^5 -alkenyltetramethylcyclopentadienyl)titanium complexes, $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]$, where $\text{R} = 1$ -methylallyl (**3a**), but-3-en-1-yl (**3b**) and pent-4-en-1-yl (**3c**), is based on a known procedure¹. The reaction of 2,3,4,5-tetramethylcyclopent-2-en-1-one with alkenyl Grignard reagents followed by iodine-catalyzed dehydration of the resulting 1-alkenyl-2,3,4,5-tetramethylcyclopent-2-en-1-ols afforded the corresponding (alkenyl)tetramethylcyclopentadienes in 60–70% yields. Addition of butyllithium and a subsequent reaction of the *in situ* generated cyclopentadienide salts with one molar equivalent of trimethylsilyl chloride or trimethyltin chloride in tetrahydrofuran gave the ring-silylated (**1a**, **1b**) and stannylated derivatives (**2a**, **2c**), respectively. Finally, the latter were reacted

with stoichiometric amounts of TiCl_4 (ref.⁸) in toluene at 80°C for 3 h to give **3a–3c** in 60–80% yields (Scheme 1).



(i) Me_3ECl (E = Si or Sn), THF
 (ii) TiCl_4 , THF

1-3	R
a	$\text{CH}(\text{Me})\text{CH}=\text{CH}_2$
b	$\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
c	$\text{CH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2$

SCHEME 1

Compounds **3a–3c** were obtained as light red crystals from hexane solutions. They were characterized by ^1H and ^{13}C NMR spectra, infrared and mass spectra. The IR and NMR spectra indicate that the alkenyl double bonds do not interact with the titanium centre. This was in the case of complex **3c** further corroborated by X-ray crystallography. Compound **3a** possesses a chiral centre at the C^1 carbon atom of its 1-methylallyl group; isolation of both enantiomers from the racemic product was not attempted. The presence of the chirality centre makes the NMR resonances of the methyl groups on the cyclopentadienyl ring diastereotopic and anisochronic. Other spectral data for **3b** and **3c** are in agreement with the data reported previously for **3b** (ref.¹).

Crystal Structure of **3c**

The molecular structure of complex **3c** shows that the pentenyl side-chain is directed away from the titanium atom (Fig. 1) and, hence, the alkenyl substituent has only a marginal effect on the structure of the trichloro(η^5 -cyclopentadienyl)titanium(IV) skeleton. The plane formed by three chlorine atoms and the least-squares cyclopentadienyl plane are parallel within the precision of measurement ($0.14(8)^\circ$). The methyl groups are deviated from the cyclopentadienyl least-squares plane by bending outwards the titanium centre by max. $0.131(7)\text{ \AA}$ (C(21)) while the α -carbon atom of the alkenyl group is disposed from the plane by only $0.089(6)\text{ \AA}$. The bond lengths and selected bond angles for **3c** are given in Table I. The average

TABLE I
Bond distances (in Å) and selected bond angles (in °) for complex **3c**

Bond distances			
Ti–Cl1	2.240(1)	Ti–Cl2	2.245(1)
Ti–Cl3	1.240(1)	Ti–Cg ^a	2.021(4)
Ti–C1	2.348(3)	Ti–C2	2.362(4)
Ti–C3	2.349(4)	Ti–C4	2.357(4)
Ti–C5	2.361(4)	C1–C5	1.418(5)
C1–C2	1.425(5)	C1–C6	1.499(5)
C2–C3	1.415(5)	C2–C21	1.488(5)
C3–C4	1.425(5)	C3–C31	1.506(5)
C4–C5	1.426(5)	C4–C41	1.499(5)
C5–C51	1.500(5)	C6–C7	1.531(5)
C7–C8	1.522(6)	C8–C9	1.506(6)
C9–C10	1.307(7)		
Bond angles			
C11–Ti–Cl2	103.96(6)	C11–Ti–Cl3	103.23(5)
C12–Ti–Cl3	102.44(6)	C11–Ti–Cg ^a	115.1(1)
C12–Ti–Cg ^a	115.3(1)	C13–Ti–Cg ^a	115.2(1)
C1–C6–C7	109.7(3)	C6–C7–C8	112.5(3)
C7–C8–C9	114.8(3)	C8–C9–C10	126.3(4)

^a Cg denotes the centroid of the cyclopentadienyl ring.

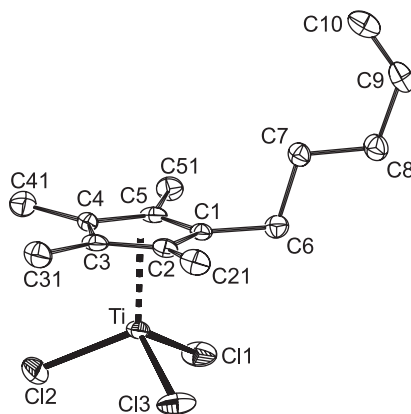


FIG. 1
ORTEP drawing of compound **3c** at the 30% probability level with the atom labelling scheme. For clarity, all hydrogen atoms are omitted

values of the Ti–Cl (2.242 Å) and Ti–C bonds (2.355 Å) compare well with the values observed for similar compounds (Table II). As there is no steric strain in compounds of this type, elongations of the bonds with respect to $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]$ likely reflect electronic effects of the substituents attached to the η^5 -cyclopentadienyl ligand. Only a large elongation of the Ti–Cl and Ti–C bond induced by *tert*-butyl substituents at the cyclopentadienyl ring may indicate some steric congestion between the chlorine atoms and *tert*-butyl groups (Table II, entry V). The data from Table II also show that the electron-releasing effect of the pentenyl group which induces elongation of both Ti–Cl and Ti–C bonds (entry VII) is similar to that of ethyl group (entry VIII) but somewhat stronger than the effect of the phenethyl group (entry VI). A similar variation in bond lengths upon methyl group replacement is also observed in the series of $[\text{TiCl}_3(\eta^5\text{-indenyl})]$ complexes (entries IX and X).

The terminal double bond in **3c**, C(9)–C(10) 1.307(7) Å, is slightly longer than that found for the 1-methylallyl group in $[\text{TiCl}_2\{\eta^5\text{-C}_5\text{Me}_4(\text{CH}(\text{Me})\text{CH}=\text{CH}_2)\}_2]$ (1.288(6) Å) (ref.¹⁷) but views of the unit cell of **3c** show that the double bond does not exert any bonding interaction with titanium atoms of neighbouring molecules in the solid state (Fig. 2).

TABLE II
Molecular parameters of trichloro(η^5 -cyclopentadienyl)titanium(IV) complexes

Entry	Cyclopentadienyl ligand	Ti–Cl _{av}	Ti–C _{av}	Ref. ^a
I	C ₅ H ₅	2.223	2.314	9
II	C ₅ H ₄ Me	2.224	2.323	10
III	1,3-C ₅ H ₃ (SiMe ₃) ₂	2.230	2.341	11
IV	C ₅ H ₄ (<i>t</i> -C ₄ H ₉)	2.232	2.342	12
V	C ₅ H ₃ (<i>t</i> -C ₄ H ₉) ₂	2.243	2.355	13
VI	C ₅ Me ₄ (CH ₂ CH ₂ Ph)	2.235	2.346	7c
VII	C ₅ Me ₄ [(CH ₂) ₃ CH=CH ₂]	2.242	2.355	This work
VIII	C ₅ Me ₄ Et	2.243	2.352	14
IX	Indenyl	2.231	2.358	15
X	Permethylinindenyl	2.237	2.370	16

^a Structural data retrieved from Cambridge Crystallographic Data Centre.

Polymerization of Styrene

Compounds **3a–3c** were mixed with excess MAO in toluene in the presence of excess styrene at molar ratios Al/Ti = 500 and 250, and the resulting systems as well as the reference systems prepared similarly from $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]$ or $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]$ were tested for their catalytic activity in the polymerization of styrene at 50 °C. For a comparison with systems containing no pendant double bonds, the systems based on complexes **4**, **5**, and **6** were also investigated at the molar ratio Al/Ti of 500. Activities of all the catalytic systems and properties of the obtained polymers are summarized in Table III. At the Al/Ti ratio of 500, the reference $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]/\text{MAO}$ system showed a much higher activity than all others. However, in accordance with the literature data¹⁸, the polymer had only a low molecular weight. The other reference system, $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]/\text{MAO}$, displayed the lowest activity, producing the syndiotactic polystyrene of high M_w . At the Al/Ti molar ratio of 250, the activity of the former reference system decreased while the latter ceased to polymerize completely. It has to be noted that the optimum activity of the $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]/\text{MAO}$ system was observed at the molar Al/Ti ratio of 4 000 (ref.¹⁹). At very low Al/Ti ratios (as used in this work) the system appeared to be inactive towards styrene while promoting polymerization of ethene²⁰. This was attributed to the formation of a Ti(IV) cationic complex which induces polymerization of ethene whereas the polymerization of styrene is assumed to proceed on Ti(III) cationic catalytic centres which are formed at higher Al/Ti ratios²¹.

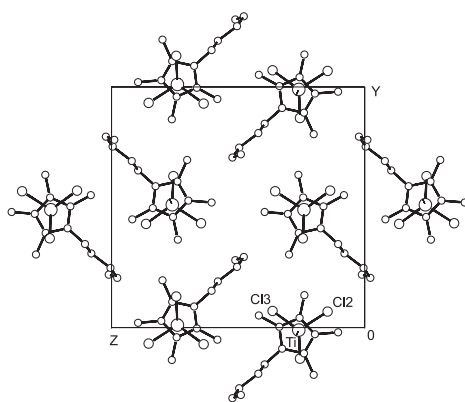


FIG. 2

View of the unit cell of **3c** along axis *x*

Among the alkenyl catalysts, the activity and the weight-average molecular weights (M_w) of the obtained polymers increase with the length of the alkenyl chain to give a maximum activity for the pentenyl-containing catalyst of 32% relative to the reference system and the molecular weight of the polymer $M_w = 3.02 \cdot 10^5$. A comparison of the systems containing complex **3b** and its saturated analogue **4** shows a retarding effect of the double bond on the polymerization rate. However, as it follows from virtually equal M_w values of the obtained polymers, the pendant double bond does not seem to play any significant role in the polymer chain transfer processes. As the unsaturated **3c**/MAO catalyst is more efficient than the saturated **4**/MAO catalyst and affords a polymer of a higher M_w , other substituent effects, e.g., polarization of the cyclopentadienyl ligand (*vide infra*), have to be considered as controlling the propagation and chain transfer polymerization steps. On the other hand, a lower activity of the **3a**/MAO system and a

TABLE III
Styrene polymerization catalyzed by the $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]/\text{MAO}$ systems^a

R	Total yield g	Monomer conversion %	$A^b \cdot 10^{-5}$	$M_w \cdot 10^{-2}$	M_w/M_n	T_m^c °C
1-Methylallyl	0.47 (0.15)	10.3 (3.4)	18.4 (6.0)	1074 (710)	2.6 (2.6)	268.1 (267.6)
But-3-en-1-yl	0.59 (0.20)	13.1 (4.4)	23.5 (7.8)	1818 (902)	2.1 (1.9)	270.8 (265.8)
Pent-4-en-1-yl	0.65 (0.24)	14.4 (5.2)	25.9 (9.4)	3022 (3084)	2.1 (2.0)	270.8 (264.5)
Butyl	0.82	18.2	32.5	1931	2.1	271.0
Phenyl	0.87	19.2	34.4	3049	2.0	270.1
4-Fluorophenyl	1.03	22.8	40.8	1930	3.8	269.9
Methyl ^d	0.10	1.8	4.0	2547	1.9	270.2
$[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]^d$	2.06 (1.40)	45.4 (31.0)	81.3 (55.4)	698 (393)	1.9 (2.0)	257.5 (258.0)

^a Polymerization conditions: $[\text{Ti}] = 5.8 \mu\text{M}$; $[\text{styrene}] = 4.36 \cdot 10^{-2} \text{ M}$ in toluene; $\text{Al/Ti} = 500$, in parentheses $\text{Al/Ti} = 250$; temperature $50 \text{ }^\circ\text{C}$; reaction time 1 h. ^b Activity: g of polymer/[mol (Ti) \times mol (styrene) \times h]. ^c Melting point of polystyrene. ^d Reference systems.

lower molecular weight of the polymer may result from the proximity of a pendant double bond or from the bulkiness of the 1-methylallyl substituent.

Of the other systems, the $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{Ph})]/\text{MAO}$ system appears to be more active than the **3c**/MAO system (42% relative to the reference system) whereas the polymers produced by both catalysts show nearly equal, maximum molecular weight and polydispersity of the polymer ($M_w = 3.05 \cdot 10^5$, $D = M_w/M_n = 2.0$). The $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4(4\text{-FC}_6\text{H}_4))]/\text{MAO}$ system showed the highest activity (50% of that of the reference system) but the resulting polymer had a broad molecular weight distribution (polydispersity $D = 3.8$), which points to a non-single site catalytic system.

Lowering the Al/Ti ratio to 250 leads to a general decrease in the catalytic activity, in agreement with earlier observations^{18,20}. The systems with **3a–3c** maintain the mentioned order of activities (**3a** < **3b** < **3c**) although at a lower level (Table III, values in parentheses), and also produce polymers of lower M_w , behaving similarly to the reference $[\text{TiCl}_3(\eta^5\text{-C}_5\text{H}_5)]/\text{MAO}$ system. Surprisingly, the **3c**/MAO catalytic system at the Al/Ti ratio of 250 produces a polymer which differs from that obtained with the same system at an Al/Ti ratio of 500 only by a lower melting point (T_m) and, hence, a lower crystallinity.

The above results are difficult to compare with most of the published data which were obtained at higher molar Al/Ti ratios. The most representative study of the effect of substituents at the cyclopentadienyl ligand, which was performed on $[\text{Ti}(\text{OMe})_3(\eta^5\text{-C}_5\text{H}_4\text{R})]$ complexes, revealed that $[\text{Ti}(\text{OMe})_3(\eta^5\text{-C}_5\text{Me}_4\text{Et})]$ was a more active catalyst than $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]$ (ref.²²). This contrasts with the results reported for a $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{Ph})]/\text{MAO}$ system which was a poorer catalyst than $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]/\text{MAO}$ (ref.¹⁹). A retarding effect of the phenethyl group was attributed to its steric effect or coordination of the phenyl group to the catalytic cationic centre, thus blocking access of monomer. The ligand substituent effects were also evaluated in the series of analogous complexes with 1-substituted η^5 -indenyl ligands $[\text{TiCl}_3(\eta^5\text{-C}_9\text{H}_6\text{R})]$ which showed at an Al/Ti ratio of 4 000 the following order of activities in polymerization of styrene with respect to the substituent R: Me > Et > propyl > but-3-en-1-yl > allyl > butyl > *tert*-butyl. All the indenyl systems were significantly more active than the reference $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]/\text{MAO}$ system²³. These systems are not relevant to the present study; nevertheless, the order of activities clearly excludes any significant effect of the pendant double bonds.

The present results together with literature data on $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]/\text{MAO}$ systems can be explained by a steeper activity increase in this system

with increasing Al/Ti ratio compared with the $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]/\text{MAO}$ systems. This may be related to the ease of reduction of $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]$ compounds, depending on the nature of substituent R. In the titanocene dichloride series, $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$, the first reduction potential surprisingly shifts from $E^\circ = -1.573$ V for $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ to -1.392 V for $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$ with R = Ph and 4-fluorophenyl, *i.e.*, close to the reduction potential of $[\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_4\text{Me})_2]$ (ref.²⁴). Such a large positive shift of the standard redox potential was tentatively explained by steric effect exerted by rotating cyclopentadienyl ligands (increasing the angle between the planes of cyclopentadienyl rings). However, the anisotropy of electron density in the cyclopentadienyl ring resulting from a lower symmetry of R-substituted cyclopentadienyl ligands may cause a similar effect. This suggestion is compatible with the above mentioned view that the $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]$ catalyst, which is most difficult to reduce, requires a large excess of MAO to obtain the catalytic Ti(III) cationic complex²¹. An easier reduction of probably all the $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]$ compounds investigated in this work may be a reason for their high activity in the polymerization of styrene even at low Al/Ti molar ratios. Unfortunately, standard reduction potentials of these compounds are not yet available.

Conclusions

The systems based on compounds **3a–3c** and MAO at the molar ratio Al/Ti = 500 catalyze the polymerization of styrene to syndiotactic polystyrene with their activity increasing with the length of the alkenyl chain. However, the activity of the saturated **4**/MAO system falls between the activities of **3b**/MAO and **3c**/MAO systems. Upon changing the titanium-containing component of the catalytic system, the molecular weights of the syndiotactic polymer increase in the order **3a** < **3b** < **4** < **3c**. This indicates only a small, if any, influence of the pendant double bonds on both the activity and chain transfer reaction. Much higher activities of these systems and the systems based on **5** or **6** than that of the $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_5)]/\text{MAO}$ system is tentatively accounted for by easier reduction of all these compounds to catalytic Ti(III) cationic complexes, especially at the used low Al/Ti ratio.

EXPERIMENTAL

General Conditions

Reactions with Grignard reagents and silylation or stannylation reactions were carried out under argon. Preparation of trichloro(η^5 -cyclopentadienyl)titanium(IV) complexes from stannylated cyclopentadienes and the work-up were performed under vacuum conditions on a vacuum line using all-glass devices equipped with breakable seals.

Samples for NMR spectroscopy were prepared in all-glass devices on a vacuum line and sealed off. NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^1H , 399.95; ^{13}C , 100.58 MHz) in C_6D_6 solutions at 298 K. Chemical shifts (δ in ppm) are given relative to the solvent signal (δ_{H} 7.15, δ_{C} 128.00). Coupling constants J are given in Hz. Crystals of complex **3c** for X-ray diffraction analysis were mounted into Lindemann glass capillaries under purified nitrogen in a glovebox (mBraun Labmaster 130; O_2 and H_2O contents lower than 2.0 ppm). Crystals for mass spectral measurements and melting point determination were placed into capillaries in a glovebox and sealed by flame. KBr pellets for IR spectra were prepared in a glovebox and measured under nitrogen in an air-proof cell on a Specord IR-75 spectrometer (wavenumbers in cm^{-1}). Mass spectra were measured on a VG 7070E instrument (EI, 70 eV; only important mass peaks and peaks of relative abundance higher than 6% are reported). GC-MS analyses were carried out on a Hewlett-Packard gas chromatograph (5890 series II) equipped with a capillary column SPB-1 (length 30 m; Supelco) and a mass spectrometric detector (5791 A). Melting points were determined in sealed glass capillaries under nitrogen, and are uncorrected.

Chemicals

Hexane, toluene, diethyl ether, tetrahydrofuran (THF) and C_6D_6 were refluxed with LiAlH_4 and stored as solutions of dimeric titanocene $[(\mu-\eta^5:\eta^5-\text{C}_5\text{H}_4-\text{C}_5\text{H}_4)(\mu-\text{H})_2\{\text{Ti}(\eta^5-\text{C}_5\text{H}_5)_2\}]$ (ref.²⁵) on a vacuum line. The (alkenyl)tetramethylcyclopentadiene ligands, $\text{C}_5\text{HMe}_4\text{R}$, were prepared as reported earlier¹⁷. Trimethylsilyl chloride, trimethyltin chloride (1.0 M in THF), butyllithium (1.6 M in hexane) and alkenyl chlorides or bromides (all Aldrich) were used as supplied. TiCl_4 (Aldrich) was degassed, refluxed with copper wire in a sealed ampoule, and distributed by distillation on a vacuum line. Toluene for polymerizations (Lachema, p.a.) was stripped by purified nitrogen. Methylalumoxane (MAO) supplied by Witco as 30% solution in toluene was diluted with toluene to give 1.0 M solution which was used directly for the catalytic experiments. Styrene (Kaučuk, a.s.) was stirred with CaH_2 for at least 2 days and distilled under vacuum shortly before use. Titanocene dichlorides $[\text{TiCl}_2(\eta^5-\text{C}_5\text{Me}_4\text{Ph})_2]$ (ref.²⁶) and $[\text{TiCl}_2(\eta^5-\text{C}_5\text{Me}_4(4\text{-FC}_6\text{H}_4))_2]$ (ref.²⁴) were prepared as described recently.

Complex $[\text{TiCl}_2(\eta^5-\text{C}_5\text{Me}_4\text{Bu})_2]$ was prepared by the procedure described for $[\text{TiCl}_2(\eta^5-\text{C}_5\text{Me}_4\text{Ph})_2]$ (ref.²⁶) starting from butyl bromide and 2,3,4,5-tetramethylcyclopent-2-en-1-one and characterized as follows. ^1H NMR: 1.01–1.07 (br t, 3 H, CH_2Me); 1.18–1.26 (m, 4 H, $\text{CH}_3\text{CH}_2\text{CH}_2$); 1.89, 1.97 (2 \times s, 6 H, Me_4C_5); 2.55–2.62 (m, 2 H, $\text{Me}_4\text{C}_5\text{CH}_2$). ^{13}C NMR: 13.1, 13.2 (Me_4C_5); 14.2 (CH_2Me), 23.4, 28.2, 32.2 (3 \times CH_2); 127.1 (Me_4C_5 , C- CH_3), 132.7 (Me_4C_5 , C- CH_2). The signal of the second C- CH_3 (Me_4C_5) was not found. EI-MS (130 $^\circ\text{C}$, m/z (relative abundance)): 472 ($\text{M}^{+\cdot}$; 2), 439 (11), 438 (10), 437 ($[\text{M} - \text{Cl}]^+$; 25), 297 (19), 296 (9), 295 (27), 294 (5), 260 (5), 258 (5), 227 (5), 220 (5), 219 (6), 218 (16), 217 (10), 216 (6), 178 (6), 177 (33), 135 (100), 134 (20), 133 (17), 121 (8), 119 (30), 105 (7), 91 (9), 43 (13), 41 (12). IR (KBr): 3 006 (vw), 2 983 (w), 2 958 (sh), 2 947 (vs), 2 908

(vs), 2 866 (s), 2 852 (s), 1 488 (m), 1 465 (m), 1 453 (s), 1 435 (s), 1 375 (vs), 1 159 (vw), 1 104 (m), 1 066 (w), 1 018 (m), 999 (w), 988 (w), 898 (vw), 833 (w), 814 (w), 729 (m), 657 (vw), 623 (vw), 614 (w), 587 (vw), 468 (w).

Synthesis of Compounds $[\text{TiCl}_3(\eta^5\text{-C}_5\text{Me}_4\text{R})]$, where R = Bu (**4**), Ph (**5**), and 4-FC₆H₄ (**6**)

These compounds were obtained from the corresponding titanocene dichlorides by synproportionation with TiCl_4 . In a typical procedure, a degassed mixture of $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$ (4.5 mmol), TiCl_4 (0.5 ml, 4.55 mmol), and xylene (10 ml) was heated in a sealed ampule to 130 °C for 5 h. All volatiles were distilled off at 100 °C into a trap cooled with liquid nitrogen and the residue was repeatedly extracted with hexane (50 ml). Combined extracts were concentrated *in vacuo* and the product was crystallized by slow cooling to give moisture-sensitive, orange crystalline compounds in almost quantitative yields.

Compound 4: M.p. 92 °C. EI-MS (110 °C, *m/z* (relative abundance)): 330 (M^{+} ; 5), 296 (14), 295 (8), 294 (18), 260 (12), 259 (7), 258 (30), 177 (15), 136 (10), 135 (100), 134 (30), 133 (25), 121 (10), 120 (8), 119 (54), 117 (8), 115 (7), 105 (12), 91 (23), 79 (8), 65 (6), 55 (6), 53 (7), 43 (13), 41 (22), 39 (9). ^1H NMR (C_6D_6): 0.79 (filled-in t, 3 H, CH_2Me); 1.03–1.17 (m, 4 H, $\text{Me}_4\text{C}_5\text{CH}_2\text{CH}_2$); 1.97, 2.05 (2 × s, 6 H, Me_4C_5); 2.65–2.70 (m, 2 H, $\text{Me}_4\text{C}_5\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 14.0 (CH_2Me), 14.1 (δ_{H} 1.97), 14.2 (δ_{H} 2.05) (Me_4C_5), 22.9 ($\text{Me}_4\text{C}_5\text{CH}_2\text{CH}_2\text{CH}_2$ or $\text{Me}_4\text{C}_5\text{CH}_2\text{CH}_2\text{CH}_2$), 29.2 ($\text{Me}_4\text{C}_5\text{CH}_2$), 32.2 ($\text{Me}_4\text{C}_5\text{CH}_2\text{CH}_2\text{CH}_2$ or $\text{Me}_4\text{C}_5\text{CH}_2\text{CH}_2\text{CH}_2$), 137.2, 137.9, 141.9 (C_5Me_4). IR (KBr): 2 978 (w), 2 945 (vs), 2 910 (s), 2 860 (s), 2 843 (sh), 1 482 (s), 1 454 (m), 1 427 (m), 1 380 (s), 1 363 (sh), 1 260 (w), 1 239 (vw), 1 097 (w), 1 072 (w), 1 020 (s), 996 (w), 980 (vw), 792 (m), 755 (m), 745 (m), 567 (vw), 500 (m), 463 (vs).

Compound 5: EI-MS (130 °C, *m/z* (relative abundance)): 352 (6), 350 (M^{+} ; 7), 314 (6), 279 (5), 198 (15), 197 (100), 182 (10), 181 (9), 167 (12), 166 (10), 165 (17), 155 (6), 152 (6), 141 (6), 115 (7), 91 (10), 77 (6), 55 (10), 41 (8). ^1H NMR (C_6D_6): 1.93, 2.14 (2 × s, 6 H, Me_4C_5); 7.03–7.32 (m, 5 H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 14.1, 15.2 (Me_4C_5); 128.5, 128.7, 130.7 (Ph, CH); 133.4, 135.8, 138.2, 142.4 (Ph and C_5Me_4 , C_{ipso}). IR (KBr): 3 054 (w), 2 980 (w), 2 955 (m), 2 912 (m), 2 842 (w), 1 600 (vw), 1 475 (s), 1 444 (m), 1 427 (m), 1 379 (s), 1 333 (w), 1 260 (m), 1 182 (w), 1 075 (m), 1 022 (s), 839 (vw), 798 (m), 760 (s), 700 (s), 670 (w), 645 (vw), 592 (w), 505 (m), 467 (vs), 450 (s).

Compound 6: M.p. 143 °C. EI-MS (140 °C, *m/z* (relative abundance)): 370 (6), 368 (M^{+} ; 8), 332 (5), 216 (21), 215 (100), 214 (7), 200 (12), 199 (13), 185 (12), 184 (13), 183 (14), 173 (7), 165 (8), 159 (6), 133 (7), 119 (6), 109 (8), 83 (6), 81 (6), 69 (10), 57 (13), 55 (15), 43 (12), 41 (17), 39 (7). ^1H NMR (C_6D_6): 1.92, 2.06 (2 × s, 6 H, Me_4C_5); 6.71–6.78 (m, 2 H, C_6H_4); 7.04–7.10 (m, 2 H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 14.1, 15.1 (Me_4C_5); 115.6 (d, $^2J_{\text{FC}} = 21$, $\text{C}_6\text{H}_4\text{F}$, $\gamma\text{-CH}$), 129.2 (d, $^4J_{\text{FC}} = 3$, $\text{C}_6\text{H}_4\text{F}$, $\alpha\text{-C}$), 132.6 (d, $^3J_{\text{FC}} = 9$, $\text{C}_6\text{H}_4\text{F}$, $\beta\text{-CH}$), 135.7, 138.2, 141.0 (Me_4C_5 , C_{ipso}); 162.9 (d, $^1J_{\text{FC}} = 250$, $\text{C}_6\text{H}_4\text{F}$, $\delta\text{-CF}$). IR (KBr): 3 060 (vw), 3 045 (vw), 2 989 (vw), 2 959 (w), 2 913 (w), 2 845 (vw), 1 602 (m), 1 514 (s), 1 477 (s), 1 424 (m), 1 380 (s), 1 300 (vw), 1 260 (w), 1 231 (vs), 1 160 (s), 1 100 (m), 1 017 (s), 994 (sh), 852 (vs), 824 (s), 798 (w), 749 (m), 669 (vw), 590 (m), 561 (m), 525 (w), 488 (s), 458 (vs).

Synthesis of 5-Alkenyl-1,2,3,4-tetramethyl-5-(trimethylsilyl)cyclopenta-1,3-dienes
(**1a** and **1b**)

In general, the cyclopentadienide anion formed by addition of BuLi to the respective alkenylcyclopentadiene in THF was reacted with an excess of trimethylsilyl chloride. The procedure is described in detail for compound **1a**.

Butyl lithium (48 mmol, 30 ml of 1.6 M solution in hexane) was added to a solution of 1,2,3,4-tetramethyl-5-(1-methylallyl)cyclopenta-1,3-diene (8.30 g, 47 mmol) in THF (500 ml) and the obtained red solution was stirred for 3 h. Trimethylsilyl chloride (6.50 g, 60 mmol) was slowly added, the resulting pale yellow solution stirred for 30 min and then most of the solvent was distilled off. Finally, all volatiles were distilled off under vacuum of a rotary pump at a temperature not exceeding 60 °C. The yield of a remaining yellow liquid was 5.6 g (48%).

1,2,3,4-Tetramethyl-5-(1-methylallyl)-5-(trimethylsilyl)cyclopenta-1,3-diene (1a). GC-MS (*m/z* (relative abundance)): 248 (M^{+} ; 21), 233 (8), 175 (10), 174 (22), 161 (11), 160 (9), 159 (48), 145 (14), 133 (8), 129 (10), 128 (8), 119 (7), 117 (7), 115 (7), 105 (8), 91 (10), 73 (100), 59 (6), 45 (20), 43 (7). IR (neat): 3 070 (m), 2 950 (s), 2 910 (s), 2 860 (s), 1 810 (w), 1 630 (m), 1 450 (s), 1 405 (m), 1 370 (m), 1 260 (m), 1 245 (s), 1 065 (w), 990 (m), 905 (s), 835 (vs), 750 (m), 680 (m), 625 (m).

1-(But-3-en-1-yl)-2,3,4,5-tetramethyl-5-(trimethylsilyl)cyclopenta-1,3-diene (1b) (6.2 g) was obtained from the same amounts of reagents (yield 53%). GC-MS (*m/z* (relative abundance)): 248 (M^{+} ; 10), 175 (23), 159 (12), 145 (8), 133 (7), 119 (12), 105 (7), 91 (15), 77 (6), 74 (9), 73 (100), 69 (7), 59 (8), 55 (9), 45 (27), 43 (14), 41 (11). IR (neat): 3 073 (m), 2 950 (vs, b), 2 920 (vs, b), 2 857 (s), 1 637 (s), 1 443 (s, b), 1 375 (m), 1 260 (s), 1 247 (vs), 1 130 (w), 988 (m), 908 (s), 836 (vs, b), 752 (m), 680 (m), 627 (m), 585 (w), 493 (w).

Synthesis of 5-(Alkenyl)-1,2,3,4-tetramethyl-5-(trimethylstannyl)cyclopenta-1,3-dienes
(**2a** and **2c**)

Cyclopentadienide anion formed as above was reacted with trimethyltin chloride in THF. The procedure is described in detail for compound **2c**.

Butyl lithium (32 ml of 1.6 M solution in hexane, 51 mmol) was added to 1,2,3,4-tetramethyl-5-(pent-4-en-1-yl)cyclopenta-1,3-diene (9.50 g, 50 mmol) in THF (150 ml). The resulting red solution was stirred at room temperature for 1 h, trimethyltin chloride (50 ml of 1 M solution in THF, 50 mmol) was added and the formed light-yellow solution was stirred for another 1 h. THF was evaporated on a rotary evaporator, the residue was extracted with hexane (3 × 50 ml) and the combined extracts were filtered. Hexane was evaporated under reduced pressure and the crude product was distilled under vacuum of a rotary pump. An orange liquid distilling from a boiling water bath was stored under argon atmosphere. Yield: 14.0 g (79.0%).

1,2,3,4-Tetramethyl-5-(pent-4-en-1-yl)-5-(trimethylstannyl)cyclopenta-1,3-diene (2c). GC-MS (*m/z* (relative abundance)): 354 (M^{+} ; not observed), 341 (9), 340 (10), 325 (12), 299 (11), 295 (10), 207 (30), 193 (8), 191 (31), 189 (19), 187 (12), 175 (15), 174 (8), 169 (17), 167 (13), 165 ([SnMe_3] $^{+}$; 100), 164 (28), 163 (74), 162 (25), 161 (45), 159 (13), 150 (10), 148 (10), 147 (8), 145 (9), 135 (34), 134 (68), 133 (73), 132 (10), 131 (14), 129 (8), 120 (12), 119 (51), 118 (9), 117 (12), 115 (10), 105 (14), 103 (8), 91 (21), 77 (16).

1,2,3,4-Tetramethyl-5-(1-methylallyl)-5-(trimethylstannyl)cyclopenta-1,3-diene (2a) was obtained in a yield of 13.70 g (80.8%). GC-MS (*m/z* (relative abundance)): 340 (M^{+} ; 20), 338

(16), 325 (14), 323 (11), 321 (8), 295 (12), 293 (10), 291 (6), 265 (5), 176 (20), 175 (38), 174 (26), 169 (25), 167 (20), 165 ([SnMe₃]⁺; 100), 163 (99), 161 (76), 159 (38), 145 (26), 135 (21), 133 (30), 131 (17), 129 (20), 128 (17), 121 (15), 120 (11), 119 (23), 117 (15), 115 (16), 91 (24), 77 (13), 65 (6), 55 (8), 41 (8).

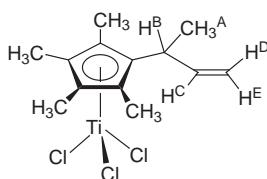
Preparation of Trichloro(η⁵-alkenyltetramethylcyclopentadienyl)titanium(IV) Complexes **3a-3c**

Compounds **3a-3c** were obtained by elimination of trimethylsilyl chloride from silylated cyclopentadienes or trimethyltin chloride from their stannylated analogues upon addition of TiCl₄ in toluene²⁷. The less frequently used procedure using a trimethylstannylated cyclopentadiene is described in detail for [η⁵-tetramethyl(pent-4-en-1-yl)cyclopentadienyl]titanium trichloride (**3c**).

1,2,3,4-Tetramethyl-5-(pent-4-en-1-yl)-5-(trimethylstannyl)cyclopenta-1,3-diene (3.2 g, 9.0 mmol) was degassed and dissolved in 10 ml of toluene. This solution was mixed with TiCl₄ (1.0 ml, 9.1 mmol) dissolved in 10 ml of toluene under vacuum at -18 °C, and the mixture was vigorously shaken and heated in a water bath at 60 °C for 15 min and then at 80 °C for 2 h. All volatiles were distilled off at 100 °C into a trap cooled with liquid nitrogen and the residue was repeatedly extracted with hexane (30 ml) in a closed system. An orange-yellow extract was concentrated to a volume of 15 ml and the solution was slowly cooled from ca 100 to 0 °C. The mother liquor was decanted, orange crystals of **3c** were washed with cold hexane and dried *in vacuo*. The mother liquor was concentrated to about 5.0 ml and crystallized as above to give a second crop of crystalline **3c**. Overall yield: 2.52 g (81%).

Trichloro[η⁵-tetramethyl(1-methylallyl)cyclopentadienyl]titanium(IV) (**3a**) and trichloro[η⁵-(but-3-en-1-yl)tetramethylcyclopentadienyl]titanium(IV) (**3b**) were obtained analogously and in similar yields.

[TiCl₃{η⁵-C₅Me₄(CH(Me)CH=CH₂)}] (**3a**). Orange crystals, yield 2.27 g (76%). M.p. 136 °C. MS (120 °C, *m/z* (relative abundance)): 330 (10), 328 (M⁺; 11), 296 (11), 295 (13), 294 (46), 293 ([M - Cl]⁺; 23), 292 ([M - HCl]⁺; 67), 258 ([M - 2 Cl]⁺; 19), 257 (12), 256 (48), 254 (13), 241 (20), 176 (14), 175 ([M - TiCl₃]⁺; 100), 160 (40), 147 (12), 145 (37), 135 (10), 133 (31), 130 (11), 129 (16), 128 (13), 121 (15), 119 (26), 117 (10), 115 (12), 105 (21), 91 (21), 77 (13), 69 (10), 55 (19), 53 (11), 41 (21), 39 (12). ¹H NMR: 1.15 (d, 3 H, ³J_{AB} = 7.2, CHCH₃ A); 1.86, 1.88, 2.07, 2.11 (4 × s, 3 H, Me₄C₅); 3.74 (tddd, 1 H, ³J_{AB} = 7.2, ³J_{BC} = 5.3, ⁴J_{BD} = ⁴J_{BE} = 1.8, CHCH₃ B); 4.82 (ddd, 1 H, ⁴J_{BD} = 1.7, ³J_{CD} = 17.3, ²J_{DE} = 1.8, =CH₂ D); 4.92 (ddd, 1 H, ⁴J_{BE} = 1.7, ³J_{CE} = 10.4, ²J_{DE} = 1.8; =CH₂ E); 5.94 (ddd, 1 H, ³J_{BC} = 5.3, ³J_{CD} = 17.3, ³J_{CE} = 10.4; -CH = C). ¹³C NMR: 13.9, 14.0, 14.6, 14.7 (Me₄C₅); 18.3 (CHCH₃), 38.0 (CHCH₃), 114.5 (=CH₂), 136.2, 136.8, 138.3, 138.4 (Me₄C₅, C-CH₃); 140.1 (-CH=), 144.0 (Me₄C₅, C-CH). IR (KBr): 3 084 (w), 2 984 (sh), 2 966 (s), 2 911 (m), 1 633 (s), 1 477 (s), 1 452 (m), 1 413 (m), 1 373 (vs), 1 173 (w), 1 015 (s), 990 (s), 915 (vs), 833 (w), 742 (s, b), 706 (w), 666 (vw), 620 (w), 580 (vw), 487 (s), 449 (vs).



$[TiCl_3(\eta^5-C_5Me_4(CH_2CH_2CH=CH_2))] (3b)$. Orange crystals, yield 2.15 g (72%). MS (120 °C, m/z (relative abundance)): 330 (5), 328 (M^{+} ; 4.6), 294 (8), 293 (6), 292 (11), 291 (9), 289 (21), 288 (6), 287 (22), 256 (11), 175 (17), 135 (12), 134 (100), 133 (20), 119 (42), 117 (6), 105 (6), 91 (13), 77 (8), 53 (5), 41 (14). 1H NMR: 1.81 (m, 2 H, $CH_2CH_2CH=CH_2$); 1.91, 1.98 (2 \times s, 6 H, Me_4C_5); 2.74 (m, $CH_2CH_2CH=CH_2$); 4.81–4.87 (m, 2 H, $=CH_2$); 5.50 (m, 1 H, $-CH=$). ^{13}C NMR: 14.0, 14.2 (Me_4C_5); 28.9 ($CH_2CH_2CH=CH_2$), 34.0 ($CH_2CH_2CH=CH_2$), 115.9 ($=CH_2$), 136.9 ($-CH=$), 137.0, 137.6 (Me_4C_5 , C- CH_3); 140.3 (Me_4C_5 , C- CH_2).

$[TiCl_3(\eta^5-C_5Me_4(CH_2CH_2CH_2CH=CH_2))] (3c)$. Orange crystals, yield 2.25 g (76%). M.p. 105 °C. MS (125 °C, m/z (relative abundance)): 346 (6), 344 (16), 342 (M^{+} ; 17), 310 (6), 309 (10), 308 (24), 307 (17), 306 (33), 302 (8), 300 (8), 289 (14), 287 (14), 272 (20), 271 (13), 270 (50), 269 (10), 268 (11), 267 (28), 266 (11), 265 (37), 264 (6), 254 (22), 253 (9), 252 (31), 227 (6), 217 (8), 216 (7), 213 (6), 189 (34), 161 (13), 159 (6), 148 (16), 147 (79), 145 (6), 135 (20), 134 (70), 133 (77), 131 (8), 121 (11), 120 (15), 119 (100), 118 (7), 117 (16), 116 (7), 115 (12), 107 (8), 105 (25), 103 (7), 93 (7), 91 (36), 83 (7), 81 (6), 79 (11), 77 (20), 69 (7), 67 (6), 65 (9), 57 (8), 55 (29), 53 (15), 51 (8), 41 (33), 39 (21). 1H NMR: 1.16 (m, 2 H, $CH_2CH_2CH_2CH=CH_2$); 1.81 (m, 2 H, $CH_2CH_2CH_2CH=CH_2$); 1.92, 2.00 (2 \times s, 6 H, Me_4C_5); 2.66 (m, 2 H, $CH_2CH_2CH_2CH=CH_2$); 4.97 (m, 2 H, $=CH_2$); 5.64 (m, 1 H, $-CH=$). ^{13}C NMR: 14.0, 14.1 (Me_4C_5); 28.9 ($CH_2CH_2CH_2CH=CH_2$), 29.3 ($CH_2CH_2CH_2CH=CH_2$), 33.7 ($CH_2CH_2CH_2CH=CH_2$), 115.5 ($=CH_2$), 136.9, 137.6 (Me_4C_5 , C- CH_3); 137.7 ($-CH=$), 141.2 (Me_4C_5 , C- CH_2). IR (KBr): 3 077 (m), 2 999 (w), 2 979 (m), 2 940 (s), 2 915 (s), 2 885 (sh), 2 864 (sh), 2 827 (m), 1 813 (vw), 1 635 (s), 1 483 (s), 1 460 (m), 1 430 (s), 1 381 (vs), 1 303 (vw), 1 258 (w), 1 104 (w), 1 017 (s), 998 (s), 908 (vs), 810 (w), 798 (w), 753 (m), 559 (m), 550 (w), 477 (vs), 450 (vs).

X-Ray Crystal Structure of Compound **3c**

A crystal fragment of **3c** was inserted into a Lindemann glass capillary under nitrogen atmosphere in a glovebox and the capillary was sealed with wax. Diffraction data were collected on an Enraf–Nonius CAD 4-MACH III diffractometer at ambient temperature using graphite monochromated $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was measured as triclinic (half of the diffraction sphere) and transformed to monoclinic after the measurement. The phase problem was solved by means of direct methods (SIR-92) (ref.²⁷) and the structure refined by full-matrix least squares on F^2 (SHELXL97) (ref.²⁸).

Crystal data for **3c**: $C_{14}H_{21}Cl_3Ti$, $M = 343.56$ g mol⁻¹, monoclinic, $P2_1/a$ (No. 14), $a = 6.632(3)$, $b = 15.249(5)$, $c = 16.105(5)$ Å; $\beta = 95.85(2)^\circ$, $V = 1\ 620(1)$ Å³, $Z = 4$, $\rho_c = 1.408$ g cm⁻³, $\mu(MoK\alpha) = 1.004$ mm⁻¹, $F(000) = 712$, crystal dimensions $0.57 \times 0.40 \times 0.30$ mm³, θ -range: 1.8–23.0°, 2 250 independent diffractions, final $R = 0.0504$, $wR = 0.1509$, GOF = 1.16, largest difference peak and hole on the final difference electron density map 0.71 and -1.05 e Å⁻³. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-164526. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

Polymerization of Styrene

The polymerization reactions were carried out at 50 °C in a 70-ml glass reactor. The reactor was equipped with a magnetic stirring bar and connected to a high vacuum line. After evacuation for 2 h, the reactor was charged in nitrogen stream with purified toluene (25 ml),

styrene (5.0 ml), 1 M MAO solution and a toluene solution of a titanium complex in this order. The mixture was then heated to 50 °C and the temperature was kept constant during the polymerization (60 min). The polymerization was quenched by addition of a mixture of aqueous HCl (5 ml of 35% HCl) and methanol (50 ml). The precipitated polymer was filtered off, washed with methanol and dried *in vacuo* at 80 °C to constant weight.

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. A4040004) and by The Ministry of Education, Youth and Sports of the Czech Republic (project No. LN00B142). The Grant Agency of the Czech Republic sponsored access to Cambridge Structure Data Base (grant No. 203/99/0067).

REFERENCES

1. Okuda J., du Plooy K. E., Toscano P. J.: *J. Organomet. Chem.* **1995**, *495*, 195.
2. Spence R. E. v. H., Piers W. E.: *Organometallics* **1995**, *14*, 4617.
3. Warren T. H., Erker G., Fröhlich R., Wibbeling B.: *Organometallics* **2000**, *19*, 127.
4. Suzuki N., Asami H., Nakamura T., Huhn T., Fukuoka A., Ichikawa M., Saburi M., Wakatsuki Y.: *Chem. Lett.* **1999**, 341.
5. Alt H. G.: *J. Chem. Soc., Dalton Trans.* **1999**, 1703.
6. Alt H. G., Jung M.: *J. Organomet. Chem.* **1999**, *580*, 1; and references therein.
7. a) Ready T. E., Chien J. C. W., Rausch M. D.: *J. Organomet. Chem.* **1999**, *583*, 11; b) Foster P., Chien J. C. W., Rausch M. D.: *Organometallics* **1996**, *15*, 4951; c) Flores J. C., Wood J. S., Chien J. C. W., Rausch M. D.: *Organometallics* **1996**, *15*, 4944.
8. Hidalgo Llinas G., Mena M., Palacios F., Royo P., Serrano R.: *J. Organomet. Chem.* **1988**, *340*, 37.
9. Engelhardt L. M., Papasergio R. I., Raston C. L., White A. H.: *Organometallics* **1984**, *3*, 18.
10. Kirschbaum K., Giolando D. M.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 2216.
11. Winter C. H., Zhou X.-X., Dobbs D. A., Heeg M. J.: *Organometallics* **1991**, *10*, 210.
12. Hart S. L., Duncalf D. J., Hastings J. J., McCamley A., Taylor P. C.: *J. Chem. Soc., Dalton Trans.* **1996**, 2843.
13. Jibril I., Abu-Orabi S., Klaib S. A., Imhof W., Huttner G.: *J. Organomet. Chem.* **1992**, *433*, 253.
14. Alcock N. W., Toogood G. E., Wallbridge M. G. H.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 598.
15. Ready T. E., Day R. O., Chien J. C. W., Rausch M. D.: *Macromolecules* **1993**, *26*, 5822.
16. O'Hare D., Murphy V., Diamond G. M., Arnold P., Mountford P.: *Organometallics* **1994**, *13*, 4689.
17. Horáček M., Štěpnička P., Gyepes R., Císařová I., Tišlerová I., Zemánek J., Kubišta J., Mach K.: *Chem. Eur. J.* **2000**, *6*, 2397.
18. a) Ishihara N., Seimiya T., Kuramoto M., Uoi M.: *Macromolecules* **1986**, *19*, 2465; b) Ishihara N., Kuramoto M., Uoi M.: *Macromolecules* **1988**, *21*, 3356.
19. Ready T. E., Day R. O., Chien J. C. W., Rausch M. D.: *Macromolecules* **1993**, *26*, 5822.
20. a) Longo P., Proto A., Zambelli A.: *Macromol. Chem. Phys.* **1995**, *196*, 3015; b) Kim J., Kim K. H., Cho J. Ch., Kwak S., Kim K. U., Hojo W., Yoon H. S., Lin D. S.: *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *11*, 1733.

21. a) Ready T. E., Gurge R., Chien J. C. W., Rausch M. D.: *Organometallics* **1998**, *17*, 5236;
b) Grassi A., Zambelli A., Laschi F.: *Organometallics* **1996**, *15*, 480; c) Grassi A., Pellecchia C., Oliva L., Laschi F.: *Macromol. Chem. Phys.* **1995**, *196*, 1093.
22. Cambell R. E., Malanga M. T.: *Metcon* **1993**, *93*, 215.
23. a) Ready T. E., Chien J. C. W., Rausch M. D.: *J. Organomet. Chem.* **1996**, *519*, 21;
b) Ready T. E., Chien J. C. W., Rausch M. D.: *J. Organomet. Chem.* **1999**, *583*, 11.
24. Langmaier J., Samec Z., Varga V., Horáček M., Mach K.: *J. Organomet. Chem.* **1999**, *579*, 348.
25. Antropiusová H., Dosedlová A., Hanuš V., Mach K.: *Transition Met. Chem. (London)* **1981**, *6*, 90.
26. Horáček M., Polášek M., Kupfer V., Thewalt U., Mach K.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 61.
27. Altomare A., Burla M. C., Camalli M., Cascarano G., Giacavazzo C., Guagliardi A. Polidori G.: *J. Appl. Crystallogr.* **1994**, *27*, 435.
28. Sheldrick G. M.: *SHELXL97, Program for Crystal Structure Refinement from Diffraction Data*. University of Göttingen, Göttingen 1997.