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Preparation of metallacyclic titanocene hydrocarbyl complexes and their use in propene polymerization reactions

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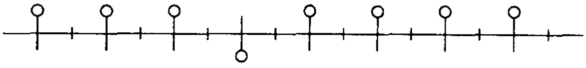
Abstract

A series of differently-substituted bis(cyclopentadienyl)titanaindan complexes has been prepared, characterized, and employed as transition metal components of homogeneous titanocene/alumoxane Ziegler-type catalysts for propene polymerization reactions. The titanaindan systems **3a** and **3b** were synthesized via an aryne titanocene intermediate by means of thermolysis of Cp_2TiPh_2 (**1a**) or $(H_3CC_5H_4)_2TiPh_2$ (**1b**) in the presence of ethylene. The analogous reactions of **1a**, **b** with propene, 1-pentene or 1-decene gave the corresponding 3-substituted 1,1-bis(cyclopentadienyl)titanaindan systems (**4a–d**). The t-butyl Cp-substituted diphenyltitanocene complexes $[(H_3C)_3CC_5H_4]CpTiPh_2$ (**1c**) and $[(H_3C)_3CC_5H_4]_2TiPh_2$ (**1d**) reacted in a different way. Their thermolysis proceeded cleanly by means of intramolecular C–H activation at the t-butyl substituent by the reactive aryne ligand to give the metallacyclic systems $(\overline{CH_2CMe_2C_5H_4)Ti}(RC_5H_4)Ph$ (**5**) (**a**: R = H; **b**: R = CMe_3). The titanaindan complex **3a** has been characterized by X-ray diffraction.

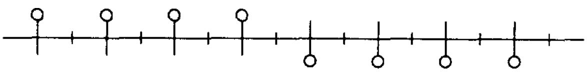
Introduction

The stereospecific polymerization of α-olefins requires definitive stereochemical features at or near the active catalytic site. Metal chirality in homogeneous metallocene/alumoxane type catalyst systems [1] can give rise to, e.g., the formation of highly isotactic polypropylene by means of "enantiomorphic site control". The resulting polymer has a very characteristic microstructure, exhibiting only singular stereochemical mistakes along the polymer chain (type I polypropylene).

Stereospecific α-olefin polymerization also sometimes takes place at active catalyst sites which are per se achiral. Here the necessary stereochemical information for the kinetic discrimination between *re* and *si* face attack comes from a carbon chirality center at the end of the growing polymer chain ("chain end control"). Such influences have been considered to be important, e.g., for the syndiospecific olefin polymerization at vanadium-containing catalyst systems [2]. In a pioneering study Ewen demonstrated that a chain end control mechanism leads to the formation of an isotactic block polymer (type II polypropylene) at homogeneous diphenyltitanocene/methylalumoxane-derived Ziegler catalyst systems over a wide temperature range (ca. −85 to −15 °C) [3].



isotactic polypropylene, type I



isotactic polypropylene, type II

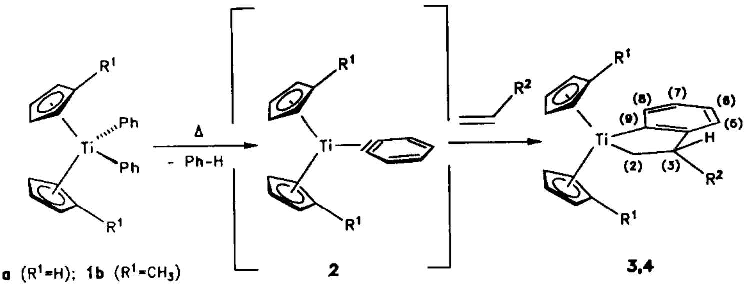
The diaryltitanocene-derived catalysts tend to become deactivated at higher temperatures by as yet unknown processes. This may be due to decomposition of the catalytic species itself [4]. Alternatively, it is conceivable that competing stoichiometric reactions of the diarylmetallocene precursor with, e.g., the added alumoxane activator becomes dominant with increasing temperature at the expense of the catalytically active species formed. Thus it would be desirable to have available other precursors for the active titanocene-derived homogeneous propene polymerization catalysts in addition to the simple diaryltitanocene complexes.

Unfortunately, many simple dialkyltitanocenes are not sufficiently thermally stable to be useful catalyst precursors [5]. However, it is well established that the Group 4 diarylmetallocenes readily generate very reactive (η^2-aryne)metallocenes upon thermolysis, and that these then can be trapped by a suitable reagent [6]. Thermally stable metallacyclic systems can be obtained by this route by use of olefinic substrates [7] or suitably placed C–H bonds as trapping agents [8]. We here describe the preparation and characterization of a variety of such metallacyclic titanium complexes derived from several Cp-substituted $(RCp)_2Ti(C_6H_5)_2$ starting materials. In a preliminary series of experiments these metallacyclic titanocene complexes were tested for their use as starting materials for the generation of active metallocene/alumoxane type propene polymerization catalysts by comparison with the corresponding non-cyclic $(RCp)_2Ti(C_6H_5)_2$ systems.

Results and discussion

Synthesis of metallacyclic aryltitanocenes

Four differently substituted diaryltitanocenes $(R^1Cp)(R^2Cp)TiPh_2$ [**1**; $R^1 = R^2 = H$ (**a**), methyl (**b**), t-butyl (**c**); $R^1 = H$, $R^2 =$ t-butyl (**d**)] were used as starting materials. Complex **1a**, which was used previously as a catalyst precursor for the metallocene/alumoxane-induced propene polymerization, was included in our study for the purpose of comparison and calibration of the reaction conditions. Cp_2TiPh_2 was conventionally prepared from titanocene dichloride and phenyllithium [9]. Similarly, (methyl-Cp)$_2$TiPh$_2$ [10] and (t-butyl-Cp)$_2$TiPh$_2$ were obtained by treating $(MeCp)_2TiCl_2$ and $(Me_3CCp)_2TiCl_2$, respectively, with PhLi in diethyl ether. The Cp-monosubstituted diarylmetallocene complex **1d** was synthesized from mono(η-cyclopentadienyl)titanium trichloride [11] by treatment with a molar equivalent of t-butylcyclopentadienyllithium (which in turn was obtained from the



R^1	R^2	compound	yield (%)
H	H	**3a**	79
H	CH_3	**4a**	71
H	n-butyl	**4b**	55
H	n-octyl	**4c**	86
CH_3	H	**3b**	73
CH_3	CH_3	**4d**	69

Scheme 1.

reaction of 6,6-dimethylfulvene with methyllithium [12]), followed by substitution of both remaining chloride ligands by treatment with PhLi.

The diphenyltitanocenes **1** were used as starting materials for the preparation of a variety of metallacyclic titanocene compounds each containing two metal to carbon σ-bonds, namely a metal to aryl-sp^2-carbon and a metal to alkyl-sp^3-carbon σ-bond. These reactions had in common that they all proceeded via thermally generated (η^2-1,2-didehydrobenzene)titanocene intermediates (**2**).

These thermally induced reactions took a straightforward course when Cp_2TiPh_2 (**1a**) or $(MeCp)_2TiPh_2$ (**1b**) were used as the starting materials. Thermolysis of **1a** in toluene solution at 80 ° C in the presence of ethylene (10 bar) cleanly produced the corresponding 1,1′-bis(cyclopentadienyl)titanaindan (**3a**), which was isolated in about 80% yield. Likewise, the Cp-substituted analogue **3b** was readily obtained from **1b** (73% isolated). 3-Substituted titanaindan systems were prepared from the parent diphenyltitanocene [products **4a** ($R = CH_3$), **4b** (R = n-butyl), and **4c** (R = n-octyl)] and the corresponding α-olefins. Trapping with propene of the aryne complex thermally generated from $(MeCp)_2TiPh_2$ (**1b**) turned out to proceed satisfactorily only at a rather high olefin pressure (35 bar); at lower pressures competing aryl(fulvene)TiCp formation [13] resulted in poor metallaindan yields and led to complex mixtures of products.

The titanaindans **4**, each bearing an alkyl substituent on the five-membered metallacyclic ring system, give very characteristic NMR spectra (see Table 1). Typically, the ^{13}C NMR signal of the methylene carbon center of **4a** adjacent to titanium [C(2)] is at δ 72.9 (^1J(CH) 122 Hz), whereas the β-carbon resonance has a smaller chemical shift value (δ 41.5, ^1J(CH) 120 Hz). The 3-substituted titanaindans **4** each have a chiral center in the five-membered ring system, and so two $^{13}C/^1H$ resonances of pairs of diastereotopic Cp-ligands are observed [**4a**: δ 114.7 and 116.2/δ 5.84 and 5.90 ppm]. The hydrogens at carbon atoms C(2) and C(3) of complex **4a** give rise to an AMX-pattern, with a marked upfield shift of the signal

Table 1

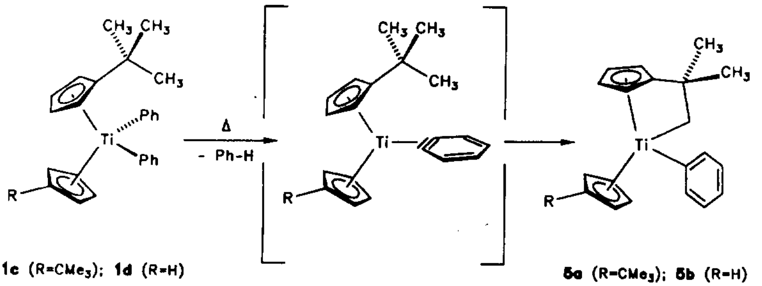
Selected ^1H and ^{13}C NMR data (δ (ppm)) for the 3-alkyltitanaindane complexes **4a**–**4d** [a]

Complex	2-H_{trans}	2-H_{cis}	3-H	8-H	C2	C3
4a	−0.26	2.95	3.57	5.73	72.9 (122)	41.5 (120)
4b	−0.26	2.94	3.53	5.71	70.1 (124)	48.0 (121)
4c	−0.22	2.97	3.55	5.70	70.1 (126)	48.0 (121)
4d	−0.16	2.69	3.57	5.84	70.0 (125)	42.3 (123)

[a] In benzene-d_6, δ-scale, ^1J(CH) in parentheses (Hz).

corresponding to the hydrogen *trans* to the methyl substituent [CH-correlation, ^1H-NOE: 2-H_{trans}: δ −0.25; 2-H_{cis}: 2.95; 3-H: 3.57 ppm; ^2J 11, $^3J_{trans}$ 11, $^3J_{cis}$ 5.5 Hz]. The observation of almost identical sets of AMX-chemical shifts and coupling constants indicates similar non-planar metallaindan structures for the complexes **4b**–**4d**, as well. We assume that the unusual chemical shift of hydrogen atom 2-H_{trans} arises from its "pseudoequatorial" position at the non-planar five-membered metallacycle, which brings it close to the σ-ligand plane of the pseudotetrahedral titanocene center. That positioning of hydrogens in the σ-ligand plane of Cp_2Ti-units in such rigid metallocene complexes gives rise to shifting of ^1H NMR signals to lower δ-numbers is substantiated by the observation that in the metallaindans the 8-H resonance is always cleanly separated from the 7–5-H multiplet [**4a**: δ 5.73 (8-H), 6.87–7.02 (7-H, 6-H, 5-H)].

The thermolysis of the Cp-t-butyl-substituted diphenyltitanocene complexes (t-butyl-Cp)$_2$TiPh$_2$ (**1c**) and (t-butyl-Cp)CpTiPh$_2$ (**1d**) takes a different course. Here intramolecular activation of a t-butyl C–H bond by the very reactive titanocene-aryne functional group is greatly predominant, and this leads to the formation of a different type of a titanacyclic ring system [8,14]. From complex **1c** we obtained the product **5a**. The chiral metallacycle was characterized from its very typical NMR spectra. Thus, the Ti-bound ring methylene group exhibits a ^1H NMR AB pattern at δ −1.94 and −0.08 ppm with a geminal proton–proton coupling constant of 10.5 Hz. There are two diastereotopic ring-methyl substituents (resonances at δ 1.06 and 1.28 ppm) and a total of 8 separate ^1H NMR signals from the methine hydrogens at the substituted Cp-moieties (δ 4.63; 5.09; 5.12; 5.51; 5.87; 5.97; 6.34; 6.83 ppm, one H each). Complex **5b**, which was formed by thermally induced Ph–H elimination and subsequent intramolecular C–H activation from **1d**, exhibited similar spectroscopic features.



1c (R=CMe$_3$); **1d** (R=H)

5a (R=CMe$_3$); **5b** (R=H)

Table 2

Selected bond parameters for the metallacycles **3a** and **6**

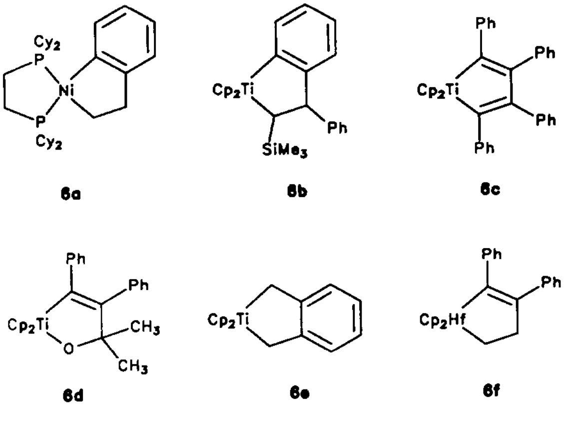
Compound	Bond distances (Å)		Bond angles (°)		Ref.
	M–C(sp^3)	M–C(sp^2)	C–M–C	M–C(sp^2)–C(sp^3)	
3a	2.197(4)	2.160(4)	78.8(2)	113.7(3)	this work
6a	1.998(9)	1.951(12)	80.9(5)	115(1)	15
6b	–	2.161(3)	81.8(1)	110.2(3)	16
6c	–	2.172(5)	80.3(2)	111.0(3)	17
6d	–	2.190(4)	78.7(1)	110.1(3)	18
6e	2.204(4)	–	76.7(2)	–	19
	2.202(5)	–	–	–	
6f	2.255(1)	2.268(4)	80.2(2)	110.6(3)	20

X-Ray crystal structure analysis of the titanaindan 3a

The molecular structure of the 1,1-bis(cyclopentadienyl)titanaindan complex (**3a**) was determined by X-ray diffraction. The titanium atom in **3a** is pseudotetrahedrally coordinated by two η-Cp rings (average Ti–C(Cp) distance 2.07 Å) and two σ-bonded carbon centers of the metallaindan framework. The Ti–C(11) bond distance is 2.160(4) Å, which is typical for a Ti–C(sp^2) bond in a five-membered titanacycle (cf. 2.161(3) for **6b** [16]; 2.172(5) for **6c** [17]; 2.190(4) Å for **6d** [18], see Table 2 and Scheme 2). The Ti–C(7) distance in **3a** is 2.197(4) Å, which is similar to those for the titanium–(sp^3)carbon σ-bonds in complex **6e** (2.204(4) and 2.202(5) Å) or bis(η-indenyl)titanium dimethyl (2.21(2) Å) [21]. The C(11)–Ti–C(17) angle is 78.8(2)°, which is within the range observed for many five-membered metallacycles (see Table 2).

Within the metallacyclic framework of **3a** we find typical C(sp^3)–C(sp^3) and C(sp^3)–C(sp^2) single bonds between carbon centers C(17)–C(18) (1.532(6) Å) and C(18)–C(12) (1.519(6) Å), respectively [22]. The lengths of the C(sp^2)–C(sp^2) bonds within the aromatic ring of **3a** are between 1.352(7) and 1.393(6) Å, except for C(11)–C(12), which is slightly longer at 1.410(6) Å.

The Ti–C(17)–C(18) and C(12)–C(18)–C(17) angles at 107.5(3) and 110.4(3)° are as expected for sp^3-hybridized ring carbon centers, as is the C(11)–C(12)–C(18)



6a **6b** **6c**

6d **6e** **6f**

Scheme 2.

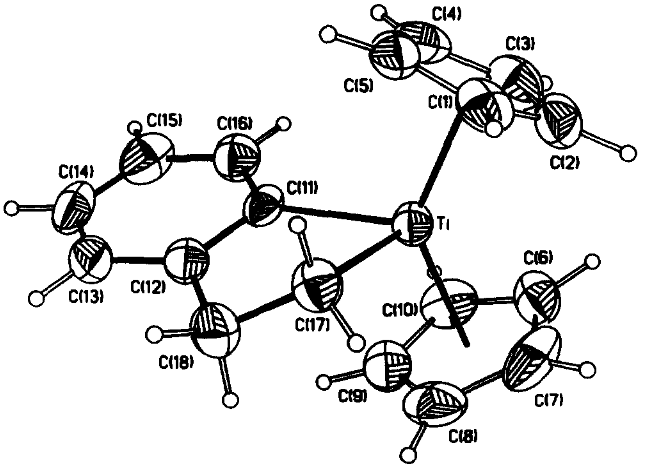


Fig. 1. A view of the molecular structure of the titanaindan **3a**.

angle (117.0(4)°) at the *sp*^{2}-carbon atom. Only the Ti–C(11)–C(12) angle (113.7(3)°) is somewhat smaller than usual. The bonding angles at the *sp*^{2}-carbon center within the five-membered metallacycles **6a**–**6e** appear to be similarly decreased (see Table 2).

As in most metallacyclopentene analogues the five-membered ring system of the titanaindan **3a** is not planar but has a distorted twist-conformation. The atoms Ti, C(11), C(12), and C(18) are close to coplanar (dihedral angle −0.35°), whereas the C(17) carbon lies 0.62 Å above the plane (the dihedral angles C(11)–C(12)–C(18)–C(17) and C(12)–C(11)–Ti–C(17) are 26.2 and −16.7°, respectively).

Table 3

Selected bond distances (Å) and angles (°) of **3a**

Ti–Cnt(1) [a]	2.068(4)	C(12)–C(13)	1.388(6)
Ti–Cnt(2)	2.072(4)	C(12)–C(18)	1.519(6)
Ti–C(11)	2.160(4)	C(13)–C(14)	1.352(7)
Ti–C(17)	2.197(4)	C(14)–C(15)	1.392(7)
Cp(C–C) av.	1.388(7)	C(15)–C(16)	1.391(6)
C(11)–C(12)	1.410(6)	C(17)–C(18)	1.532(6)
C(11)–C(16)	1.393(6)		
Cnt(1)–Ti–Cnt(2)	134.2(2)	C(11)–C(12)–C(13)	120.7(4)
Cnt(1)–Ti–C(11)	110.3(2)	C(11)–C(12)–C(18)	117.0(4)
Cnt(1)–Ti–C(17)	106.1(2)	C(13)–C(12)–C(18)	122.3(4)
Cnt(2)–Ti–C(11)	105.3(3)	C(12)–C(13)–C(14)	121.7(4)
Cnt(2)–Ti–C(17)	108.2(3)	C(13)–C(14)–C(15)	120.0(4)
C(11)–Ti–C(17)	78.8(2)	C(14)–C(15)–C(16)	118.2(4)
Ti–C(11)–C(12)	113.7(3)	C(11)–C(16)–C(15)	123.5(4)
Ti–C(11)–C(16)	130.3(3)	Ti–C(17)–C(18)	107.5(3)
C(12)–C(11)–C(16)	115.9(4)	C(12)–C(18)–C(17)	110.4(3)

[a] Cnt(1) = centroid C(1)–C(5); Cnt(2) = centroid C(6)–C(18).

Table 4

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2 \times 10^3$) for **3a**

Atom	x	y	z	U [a]
Ti	−133.0(4)	1789.2(5)	2509.5(5)	32.2(2)
C(1)	322(3)	2415(4)	3931(3)	47(2)
C(2)	−491(3)	1845(4)	4035(3)	50(2)
C(3)	−296(3)	840(4)	3835(3)	52(2)
C(4)	641(4)	778(4)	3613(3)	57(2)
C(5)	1029(3)	1742(4)	3659(3)	50(2)
C(6)	−1751(3)	1360(4)	2436(3)	54(2)
C(7)	−1666(3)	2403(5)	2303(4)	63(2)
C(8)	−1202(3)	2552(4)	1495(4)	59(2)
C(9)	−976(3)	1604(4)	1147(3)	49(2)
C(10)	−1314(3)	872(3)	1724(3)	50(2)
C(11)	879(3)	1121(3)	1621(3)	33(1)
C(12)	1314(3)	1840(3)	1059(3)	37(1)
C(13)	1955(3)	1526(4)	425(3)	45(2)
C(14)	2178(3)	527(4)	316(3)	54(2)
C(15)	1757(3)	−218(4)	842(3)	56(2)
C(16)	1123(3)	100(3)	1484(3)	46(2)
C(17)	646(3)	3154(3)	2090(3)	41(1)
C(18)	1014(3)	2951(3)	1152(3)	47(2)

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

Polymerization reactions

Propene-polymerizations were carried out with homogeneous Ziegler-type catalysts derived from the metallacyclic titanaindan complexes **3a**, **4a**, **4b**, and **4d** as well as from the metallacyclic titanocene aryls **5a** and **5b**. For purposes of comparison some propene polymerizations were also carried out with catalysts prepared from diphenyltitanocene (**1a**) [3].

The objective of this study was to find out which of the metallacyclic titanocene complexes were best suited for the generation of homogeneous olefin polymerization catalysts, and so we report here the results of some preliminary experiments aimed at obtaining general guidance in this respect. For none of the experiments described were the reaction conditions optimized, and so we have confined ourselves to qualitative and descriptive interpretations.

In each case, the organometallic titanocene catalyst precursor was activated by treatment with excess oligomeric methylalumoxane at low temperature in toluene in the presence of propene [23]. The polymerization experiments were carried out at constant temperatures between −50 and −20 °C. Molar [Ti]/[Al] ratios were typically varied between 1/14 and 1/260. The produced polypropylene was isolated and its molecular weight ($\bar{M}_\eta$) determined. The titanaindan-derived catalysts typically produced polypropylenes with molecular weights between 50,000 and 200,000 under these conditions (see Table 5). The polymer samples obtained were characterized by IR and NMR spectroscopy (see Table 5). Some qualitative information about the stereochemical composition was obtained by ^{13}C NMR spectroscopy focused on methyl pentad resonances [24].

It turned out that most of the polymers obtained were isotactic block polypropylenes (isotactic type II polypropylene, see above). This indicated dominant stereo-

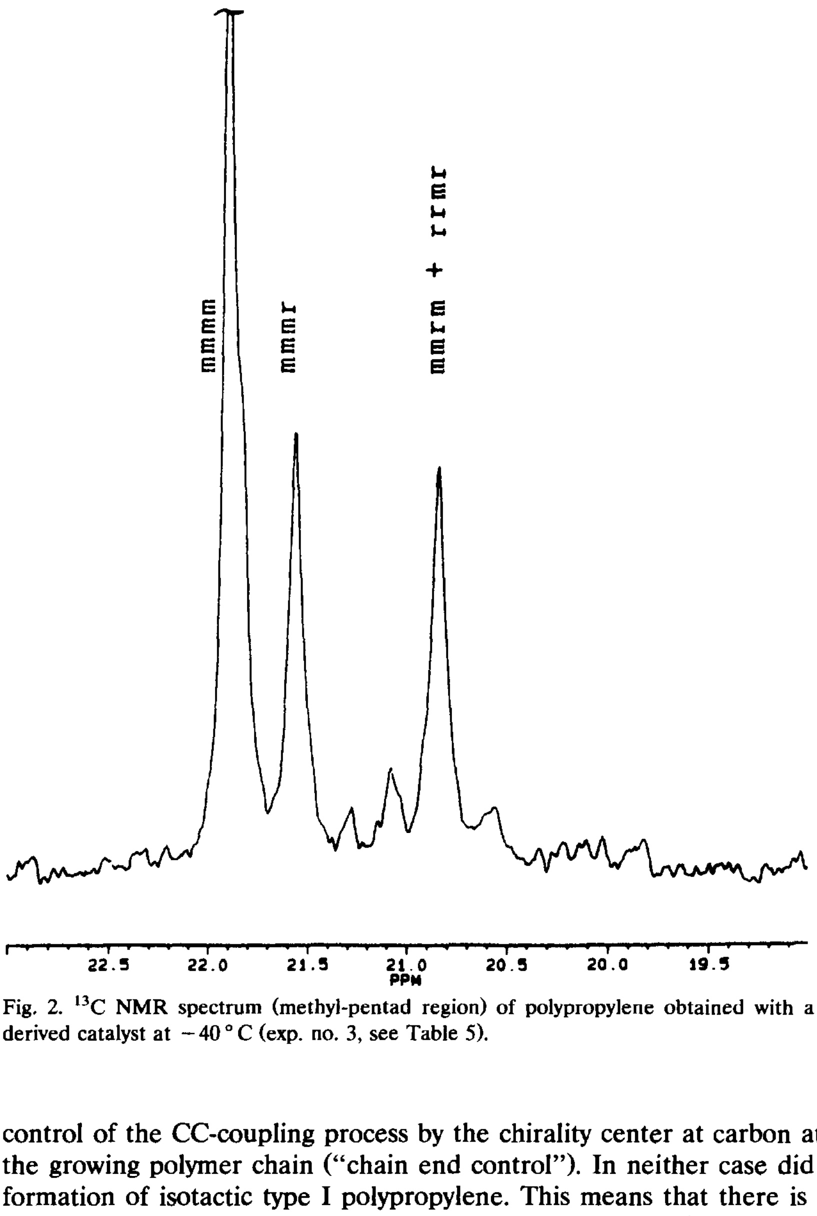


Fig. 2. ^{13}C NMR spectrum (methyl-pentad region) of polypropylene obtained with a 3a/$(MeAlO)_x$ derived catalyst at −40 °C (exp. no. 3, see Table 5).

control of the CC-coupling process by the chirality center at carbon at the end of the growing polymer chain ("chain end control"). In neither case did we observe formation of isotactic type I polypropylene. This means that there is no effective transfer of chirality from the chiral catalyst precursors (e.g. the chiral carbon centers of complexes **4a**, **4b**, **4d**, **5a** or **5b**) to the product. Probably rapid and complete loss of the chiral σ-ligands occurs during the formation of the active catalysts, and this explains why stereochemical "enantiomorphic site control" was not observed in these experiments.

Figure 2 shows the ^{13}C NMR methyl pentad signals in a typical case (see Table 5, experiment No. 3). The polymer was obtained by using a catalyst derived from the parent metallacycle bis(cyclopentadienyl)titanaindan **3a** which was activated by methylalumoxane with a [Ti]/[Al] ratio of 1/39. The CC-coupling reaction was carried out at −40 °C. Polypropylene was formed at an overall average rate of 560

Table 5

Propene polymerization reactions with homogeneous methylalumoxane/titanocene-based catalyst systems

Exp. no.	Catalyst	Ti-compl. (g)	$(\mathrm{MeAlO})_x$ (g)	Molar ratio [Ti]/[Al]	T (°C)	t (h)	Polypropylene (g)	Activity [a]	$\bar{M}_\eta$ ($\times 10^3$)	Polypropylene structure [b]	$\langle m_n \rangle_\sigma$ [c]	I [d]
1	**3a**	0.025	0.72	1/140	−40	0.3	4.3	3600	135	57/25/18	7	2.7
2	**3a**	0.040	1.52	1/180	−40	1.3	7.5	830	141	63/20/17	8	25
3	**3a**	0.027	0.20	1/40	−40	1.3	3.3	560	176	52/24/24	7	2.1
4	**4a**	0.050	1.16	1/120	−30	2.2	3.1	180	41	isotact.	[e]	[e]
5	**4a**	0.023	0.50	1/110	−40	0.8	7.3	2600	227	65/19/16	8	
6	**4a**	0.053	0.25	1/24	−40	0.5	2.0	470	223	68/10/22	9	1.8
7	**4b**	0.038	0.50	1/99	−30	0.5	2.0	940	121	isotact.	[e]	[e]
8	**4b**	0.027	0.50	1/108	−40	1.0	3.6	940	181	isotact.	[e]	2.7
9	**4b**	0.030	0.50	1/100	−50	2.0	2.4	280	227	isotact.	[e]	[e]
10	**4b**	0.085	0.50	1/34	−40	0.8	0.6	67	185	isotact.	[e]	[e]
11	**1a**	0.038	0.85	1/130	−40	0.5	6.5	2400	55	isotact.	[e]	[e]
12	**1a**	0.050	0.77	1/89	−40	0.7	5.7	1200	52	61/18/21	8	2.1
13	**1a**	0.047	0.27	1/33	−40	0.4	3.2	1350	142	isotact.	[e]	[e]
14	**1a**	0.125	0.30	1/14	−40	0.8	3.3	250	160	47/28/25	6	2.4
15	**1d**	0.043	1.02	1/160	−40	1.1	6.5	1110	[e]	isotact.	[e]	[e]
16	**4d**	0.030	0.62	1/116	−40	1.5	3.3	490	[e]	atact.	[e]	[e]
17	**5b**	0.025	0.57	1/122	−20	2.0	3.0	390	[e]	atact.	[e]	[e]
18	**5b**	0.028	0.50	1/97	−40	1.0	1.1	260	[e]	atact.	[e]	[e]
19	**5a**	0.050	1.00	1/190	−20	0.8	1.0	350	[e]	atact.	[e]	[e]
20	**5a**	0.028	1.50	1/260	−40	2.0	0.3	40	[e]	atact.	[e]	[e]

[a] g [PP]/g[Ti] h·bar. [b] By ^{13}C NMR analysis of the methyl-pentad signals: isotact. = isotactic block polymer; atact. = atactic or near to atactic; the ratios shown correspond to [mmmm]/[mmmr]/[mmrm + rrmr] ratios obtained from the integrated ^{13}C NMR methyl resonances. [c] Average lengths of the *m* dyad containing blocks as obtained from statistical analysis (Bernoullian behavior). [d] *Isotacticity index derived from the intensity ratio of the IR bonds at* $\nu = 974$ and 998 cm^{-1}. [e] Not determined.

g/g [Ti] · h. The obtained polymer had a mean molecular weight of $\overline{M}_\eta = 176{,}000$. It had an isotacticity index (I) (intensity ratio of the IR bands at 974/998 cm^{-1}) [25] of about 2.1. The ^{13}C NMR spectrum featured three prominent methyl resonances that could be attributed to the mmmm, mmmr, and mmrm pentad sequences. The three signals were in an intensity ratio of 52/24/24, which fulfils the 1/1 intensity ratio requirement of the mmmr/mmrm pentad signals necessary for the type II isotactic block polymer formed by effective "chain end" stereocontrol [3]. For this polymer an average length of the isotactic blocks was calculated as $\langle m_n \rangle_\sigma = 6.7$, i.e. on average containing 6 to 7 monomer units.

The results of a variety of similarly representative polymerization reactions involving the different catalyst precursors described in the first section of this paper are listed in Table 5. These experiments show that metallacyclic titanocene complexes derived from thermally-induced reactions of diaryltitanocene complexes are suited to serve as precursors for the generation of active homogeneous propene polymerization catalysts. Many of these catalyst systems produce isotactic block polymers in the applied temperature range and exhibit reactivities and selectivities similar to those of the previously described Cp_2TiPh_2 derived catalyst system [3]. This probably indicates that the same, or at least very similar, catalytically active species are generated in all the titanocene/methylalumoxane systems mentioned above. Therefore, the thermally stable metallacycles **3–5** and derivatives thereof could be suitable starting materials for investigation of the means by which catalyst deactivation takes place in such Ti/Al-systems at elevated temperatures, and for development of ways of avoiding such as yet unidentified undesired reaction pathways.

Experimental

Organometallic compounds were prepared and handled under argon. Dried and freshly distilled solvents were used. Cp_2TiPh_2 (**1a**) and $(MeCp)_2TiPh_2$ (**1b**) were prepared by published procedures [9,10]. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP 200 SY NMR spectrometer and infrared spectra on a Nicolet 5-DXC FT IR spectrometer. Melting points (uncorrected) were determined with samples sealed under argon. Elemental analyses were carried out at Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, or the Institut für Anorganische Chemie der Universität Würzburg. Molecular weights of polypropylene samples were determined with a Schott A VS 440 Viscometer and thermostat using an Ubbelohde-Viscometer with a calibrated capillary insert (Schott). From the experimentally determined viscosity number $[\eta]$ (at extrapolated zero polymer concentration) the $\overline{M}_\eta$ molecular weight was calculated by use of the Mark–Houwink equation $k(\overline{M}_\eta)^\alpha = [\eta]$ with $\alpha = 0.8$ and $k = 1.1 \cdot 10^{-4}$ (for polypropylene at 135 ° C in decalin).

(η-Cyclopentadienyl)trichlorotitan was prepared by modification of a published procedure [11]. A solution of 8.3 g (0.033 mol) Cp_2TiCl_2 and 3.0 g (0.022 mol) of SO_2Cl_2 in 50 mL of thionyl chloride was stirred for 3 h at 90 ° C. Then another 3 g of SO_2Cl_2 were added and the mixture was refluxed for a further 3 h. The solution was then reduced to about one half of its volume and then set aside for several days at -25 ° C to allow crystallization. Solvent was decanted from the voluminous orange precipitate, which was washed with 50 mL of pentane and then with ether

(50 mL). The residue was pulverized and heated for several hours *in vacuo* at 50 °C to give 5.9 g (83%) of $CpTiCl_3$ (m.p. 210 °C). Sublimation (100–120 °C, oil diffusion pump vacuum) gave 5.2 g; Anal. Found: C, 27.95; H, 2.31. $C_5H_5Cl_3Ti$ (219.3) calc.: C, 27.38; H, 2.30%. ^1H NMR ($CDCl_3$, relative to TMS): δ 7.03 (s, Cp) ppm. ^{13}C NMR ($CDCl_3$, relative to TMS): δ 123.4 (Cp) ppm.

(η-t-Butylcyclopentadienyl)(η-cyclopentadienyl)dichlorotitan

To a solution of 5.2 g (0.024 mol) of $CpTiCl_3$ in 100 mL of diethyl ether was added dropwise at −78 °C a solution of 3.05 g (0.024 mol) of t-butylcyclopentadienyllithium in 50 mL of the ether. The red mixture was allowed to warm very slowly to room temperature and then stirred for an additional hour. Solvent was removed *in vacuo*, and the residue extracted with 400 mL of methylene chloride. The extract was filtered and concentrated *in vacuo*, and the product then allowed to crystallize at −25 °C. The crystalline $(Me_3CCp)CpTiCl_2$ was collected by filtration. Yield 4.95 g (69%), m.p. 195 °C. Anal. Found: C, 54.48; H, 5.84. $C_{14}H_{18}Cl_2Ti$ (305.1) calc.: C, 55.12; H, 5.95%. ^1H NMR ($CDCl_3$): δ 1.30 (s, 9 H, $C(CH_3)_3$), 6.47, 6.61 (m, 2H each, $Me_3C\text{-}C_5H_4$), 6.56 (s, 5H, Cp) ppm. ^{13}C NMR ($CDCl_3$): δ 31.0 (^1J(CH) 126 Hz) and 34.4 (t-butyl), 118.4, 119.2, 149.5 ($R\text{-}C_5H_4$), 120.1 (Cp) ppm.

(η-t-Butylcyclopentadienyl)(η-cyclopentadienyl)diphenyltitan (1d)

The preparation of **1d** from $(Me_3C\text{-}Cp)CpTiCl_2$ was carried out in the way described for Cp_2TiPh_2 from Cp_2TiCl_2 [9]. From 3.3 g (0.011 mol) of $(Me_3C\text{-}Cp)CpTiCl_2$ and 29 mL of a 0.75 molar ethereal phenyllithium solution were obtained 2.1 g (50%) of $(Me_3C\text{-}Cp)CpTiPh_2$ (**1d**) after crystallization at −78 °C. M.p. 111 °C (dec.). Anal. Found: C, 78.43; H, 7.36. $C_{26}H_{28}Ti$ (388.4) calc.: C, 80.40; H, 7.27%. ^1H NMR (benzene-d_6): δ 0.76 (s, 9H, $C(CH_3)_3$), 5.85, 6.17 (m, 2H each, $R\text{-}C_5H_4$), 5.89 (s, 5H, Cp), 6.68–7.04 (m, 10H, Ph) ppm. ^{13}C NMR (benzene-d_6): δ 30.8, 32.9 (t-butyl), 115.2, 116.4, 140.7 ($R\text{-}C_5H_4$), 116.1 (Cp), 124.4, 126.3, 136.5, 191.8 (Ph) ppm.

Bis(η-t-butylcyclopentadienyl)diphenyltitan (1c)

By analogy with a published procedure for Cp_2TiPh_2 (see above), $(Me_3C\text{-}Cp)_2TiPh_2$ (**1c**) was obtained by reacting 3.2 g (8.86 mmol) of $(Me_3C\text{-}Cp)_2TiCl_2$ with 23 mL of a 0.85 molar ethereal solution of phenyllithium. Crystallization at −25 °C gave 3.0 g (76%) of the product **1c**, m.p. 106–109 °C (dec.). Anal. Found: C, 81.84; H, 8.10. $C_{30}H_{36}Ti$ (444.5) calc.: C, 81.06; H, 8.16%. ^1H NMR (benzene-d_6): δ 0.86 (s, 18H, t-butyl), 6.10, 6.42 (m, 4H each, $R\text{-}C_5H_4$), 6.94–6.96 (m, 6H, Ph), 7.08–7.10 (m, 4H, Ph) ppm. ^{13}C NMR (benzene-d_6): δ 31.1, 33.3 (t-butyl), 115.4, 116.7, 140.0 ($R\text{-}C_5H_4$), 124.5, 125.6, 137.2, 191.9 (Ph) ppm.

1,1-Bis(η-cyclopentadienyl)titanaindan (3a)

A glass tube was charged with a solution of 1.65 g (4.97 mmol) of bis(η-cyclopentadienyl)diphenyltitan **1a** in 50 mL of toluene and transferred to a 300 mL autoclave. The autoclave was pressurized at ambient temperature with 8 bars of ethylene and then heated at 80 °C with stirring for 6 h. After cooling to room temperature and depressurization, the brown reaction mixture was filtered and the solvent removed *in vacuo*. The residual brown-red oil was dissolved in ca. 100 mL

Table 6

Crystal data and details of the data collection and refinement for titanaindan **3a**

Crystal parameters	
Formula	$C_{18}H_{18}Ti$
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	14.364(4)
b (Å)	13.046(4)
c (Å)	15.067(5)
V (Å^3)	2823(1)
Z	8
$d_{calc.}$ (g cm^{-3})	1.33
μ (cm^{-1})	6.1
Size (mm)	0.35 × 0.40 × 0.42
Color	dark red
T (°C)	23
Data collection	
Diffractometer	Nicolet R3m/μ
Radiation	Mo-K_α (λ 0.71073 Å)
Monochromator	graphite
Scan limits (°)	$4 \leq 2\theta \leq 48$
Scan method	ω
Reflections collected	2508
Independent reflections	2210
Independent reflections, $F_o^2 \geq 5\sigma(F_o^2)$	1320
Standard reflections	3 std/197 rflns
Decay	$\leq 1\%$
Refinement	
$R(F)$ (%)	3.88
$wR(F)$ (%)	4.28
GOF	1.136
Data/parameter	7.67
Δ/σ	0.007
$\Delta(p)$ (e Å^{-3})	0.28

of pentane and the product crystallized at −25 °C. Yield of **3a**: 1.10 g (79%), m.p. 87 °C (dec.). Anal. Found: C, 76.88; H, 6.49. $C_{18}H_{18}Ti$ (282.2) calc.: C, 76.61; H, 6.43%. IR (KBr): ν 3100, 1410, 1096, 805 (Cp), 3040, 3028, 1562, 1498, 755 (arom.), 2960, 1449, 735, 728 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.45, 3.23 (m, 2H each, CH_2CH_2), 5.84 (s, 10H, Cp), 5.89 (dd, 1H, 8-H), 6.87–6.95 (m, 3H, arom.) ppm. ^{13}C NMR (benzene-d_6 Gated, DEPT): δ 38.8 (^1J(CH) 124 Hz, C3), 60.1 (^1J(CH) 127 Hz, C2), 115.2 (Cp), 124.2, 126.1, 133.9, 147.5, 193.8 (arom. C) ppm.

Crystallographic structural characterization of the titanaindan 3a

Crystal data and details of the collection and refinement of data for $C_{18}H_{18}Ti$ are given in Table 6. Deep red crystals of $C_{18}H_{18}Ti$ were grown from pentane and attached to fine glass fibers with epoxy cement. From systematic absences the compound was assigned the orthorhombic space group *Pbca*. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with

$20° \leq 2\theta \leq 25°$. Intensity data were empirically corrected for absorption. 216 data were used to fit a six-parameter ellipsoid model ($T_{max}/T_{min} = 0.713/0.691$).

The structure was solved by direct methods. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and refined with idealized isotropic contributions (d(C–H) = 0.96 Å, $U = U_{iso}$ of attached C). The computer programs used in data collection and refinement were part of the Nicolet (Madison, WI) program packages P3 SHELXTL (version 5.1), and XP. Tables 3 and 4 list atomic coordinates and selected bond distances and angles, respectively [26].

Reaction of diphenyltitanocene (1a) with propene

As described above for the preparation of **3a** a solution of 4.1 g (12.3 mmol) of Cp_2TiPh_2 (**1a**) in 50 mL of toluene was heated for 6 h at 80 °C with 6 bar of propene. The brownish mixture was filtered and the solvent removed *in vacuo*. The residue was dissolved in 100 mL of pentane, and the product **4a** separated as a brown amorphous powder at −78 °C. Yield 2.6 g (71%), m.p. 87 °C (dec.). Anal. Found: C, 76.72; H, 7.05. $C_{19}H_{20}Ti$ (296.3) calc.: C, 77.03; H, 6.81%. IR (KBr): ν = 3100, 1424, 1101, 812 (Cp), 3040, 3031, 1566, 766 (arom)., 2961, 1444, 1360, 737, 723 cm^{-1}. ^1H NMR (benzene-d_6, assignments based on C,H-correlation and NOE): δ −0.26 (dd, ^2J 11, ^3J 5.5 Hz, 1H, 2-H_{trans}), 1.29 (d, ^3J 6.5 Hz, 3H, CH_3), 2.95 (t, $^2J = {}^3J$ = 11 Hz, 1H, 2-H_{cis}), 3.57 (m, 1H, 3-H), 5.84 (s, 5H, Cp), 5.90 (s, 5H, Cp), 5.73 (d, ^3J 7 Hz, 1H, 8-H), 6.87–7.02 (m, 3H, arom.) ppm. ^{13}C NMR (benzene-d_6, C,H-correlation in CD_2Cl_2): δ 22.4 (^1J(CH) 126 Hz, CH_3), 41.5 (^1J(CH) 120 Hz, C3), 72.9 (^1J(CH) 122 Hz, C2), 114.7, 116.2 (Cp), 124.2, 124.6 (double intensity), 132.8, 152.9, 193.1 (arom. C) ppm.

1,1-Bis(η-cyclopentadienyl)-3-n-butyltitanaindan (4b)

A solution of 2.0 g (6.0 mmol) of diphenyltitanocene **1a** and 0.8 mL (6.4 mmol) of 1-hexene in 100 mL of toluene was heated for 3 h at 80 °C. Solvent was then removed in vacuo and the residual oil dissolved in 30 mL of diethyl ether. After several days at −78 °C crystals of **4b** were obtained. After addition of ca. 30 mL of pentane to the mother liquid, more **4b** crystallized out at −25 °C. Combined yield 1.15 g (55%), m.p. 78 °C (dec.). Anal. Found: C, 77.22; H, 7.80. $C_{22}H_{26}Ti$ (338.3) calc.: C, 78.10; H, 7.75%. IR (KBr): ν = 3107, 3087, 3040, 3032, 2950, 1564, 1467, 1420, 1370, 1100, 815, 746, 730, 726 cm^{-1}. ^1H NMR (benzene-d_6): δ −0.26 (dd, ^2J 11, ^3J 5.5 Hz, 1H, 2-H_{trans}), 1.01 (t, 3H, CH_3), 1.23–1.49 (m, 5H) and 2.01 (m, 1H, n-butyl-CH_2), 2.94 (t, $2J = {}^3J$ = 11 Hz, 1H, 2-H_{cis}), 3.53 (m, 1H, 3-H), 5.85 (s, 5H, Cp), 5.92 (s, 5H, Cp), 5.71 (dd, ^3J 7, ^4J 1.5 Hz, 1H, 8-H), 6.87–7.06 (m, 3H, arom.) ppm. ^{13}C NMR (benzene-d_6): δ 14.6 (CH_3), 23.7, 29.3 and 37.3 (n-butyl-CH_2), 48.0 (^1J(CH) 121, C3), 70.1 (^1J(CH) 124 Hz, C2), 114.7 and 116.2 (Cp), 124.2 (double intensity), 124.5, 132.9, 152.4, 194.3 (arom. C) ppm.

1,1-Bis(η-cyclopentadienyl)-3-n-octyltitanaindan (4c)

A solution of 1.95 g (5.9 mmol) of Cp_2TiPh_2 and 1.1 mL (6.4 mmol) of 1-decene in 100 mL of toluene was heated for 4 h at 80 °C. Removal of solvent in vacuo at 80 °C left **4c** as a red oil (2.0 g, 86%). It was identified from its characteristic NMR spectra. ^1H NMR (benzene-d_6): δ −0.22 (dd, ^2J 11, ^3J 5.6 Hz, 1H, 2-H_{trans}), 0.92

(t, 3H, CH_3), 1.31–1.40 (m, 13H) and 2.03 (m, 1H, n-octyl-CH_2), 2.97 (t, $^1J = {}^3J = 11$ Hz, 1H, 2-H_{cis}), 3.55 (m, 1H, 3-H), 5.87 (s, 5H, Cp), 5.94 (s, 5H, Cp), 5.70 (dd, ^3J 7, ^4J 1.7 Hz, 1H, 8-H), 6.85–7.07 (m, 3H, arom.) ppm. ^{13}C NMR (benzene-d_6): δ 14.4 (CH_3), 23.1, 27.0, 29.9, 30.4, 30.7, 32.4, 37.6 (n-octyl-CH_2), 48.0 (^1J(CH) 121 Hz, C3), 70.1 (^1J(CH) 126 Hz, C2), 114.6, 116.2 (Cp), 124.1 (double intensity), 124.5, 132.9, 152.5, 194.3 (arom. C). MS: $m/z = 394$ (M^+), 254, 178 (Cp_2Ti^+) ppm.

Reaction of bis(η-methylcyclopentadienyl)diphenyltitan with ethylene

As described above for the preparation of **3a** a solution of 1.2 g (3.3 mmol) of $(MeCp)_2TiPh_2$ (**1b**) in 50 mL of toluene was heated in an autoclave for 6 h at 80 ° C with ethylene (10 bar). The brown mixture was then filtered and the solvent removed *in vacuo*. The residual oil was dissolved in 25 mL of pentane and the product **3b** crystallized at −25 ° C. Yield 0.75 g (73%), m.p. 88 ° C (dec.). Anal. Found: C, 76.40; H, 7.29. $C_{20}H_{22}Ti$ (310.3) calc.: C, 77.42; H, 7.15%. IR (KBr): $\nu = 3099$, 3089, 3029, 2939, 1564, 1497, 1444, 1430, 1380, 1100, 830, 817, 739, 716 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.36 (m, 2H, 2-H), 1.70 (s, 6H, CH_3), 3.23 (m, 2H, 3-H), 5.57, 5.62, 5.77, 5.86 (m, 2H each, R-C_5H_4), 5.99 (dd, ^3J 7, ^4J 1.5 Hz, 8-H), 6.85–6.95 (m, 3H, arom.) ppm. ^{13}C NMR (benzene-d_6): δ 15.4 (CH_3), 38.6 (^1J(CH) 127 Hz, C3), 57.5 (^1J(CH) 127 Hz, C2), 112.0, 113.2, 116.6, 117.7, 125.5 (R-C_5H_4), 123.7 (double intensity), 124.2, 126.1, 134.3, 148.8, 194.4 (arom. C) ppm.

*1,1-Bis(η-methylcyclopentadienyl)-3-methyltitanaindan (**4d**)*

By the general procedure described above, an autoclave was charged with a solution of 1.02 g (2.83 mmol) of $(MeCp)_2TiPh_2$ (**1b**) in 50 mL of toluene and then cooled to −78 ° C and propene was condensed in about 15 min. Heating of the sealed autoclave to 80 ° C gave a total pressure of 35 bar. The autoclave was kept at 80 ° C for 2 h then cooled to room temperature and depressurized. The brown mixture was filtered and the solvent removed *in vacuo*. The resulting oil was dissolved in ca. 25 mL of ether, and the product **4d** crystallized from the solution during several days at −25 ° C. Yield 0.63 g (69%), m.p. 82 ° C (dec.). Anal. Found: C, 76.56; H, 7.72. $C_{21}H_{24}Ti$ (324.3) calc.: C, 77.78; H, 7.46%. IR (KBR): $\nu = 3101$, 3090, 3038, 2950, 1560, 1498, 1444, 1420, 1375, 1096, 808, 764, 730, 724 cm^{-1}. ^{1}H NMR (benzene-d_6): δ −0.16 (dd, ^2J 11, ^3J 5.6 Hz, 1H, 2-H_{trans}), 1.25 (d, 3H, CH_3), 1.43 and 1.95 (each s, 3H, H_3C-Cp), 2.69 (t, $^2J = {}^3J = 11$ Hz, 1H, 2-H_{cis}), 3.57 (m, 1H, 3-H), 5.19 (m, 1H), 5.60, 5.68, 5.94 (m, each 2H), 6.12 (m, 1H, R-C_5H_4), 5.84 (dd, ^3J 7 Hz, 1H, 8-H), 6.82–6.93 (m, 2H), 6.98 (dd, 1H, arom.) ppm. ^{13}C NMR (benzene-d_6): δ 15.1 and 15.8 (H_3C-Cp), 23.7 (CH_3), 42.3 (^1J(CH) 123 Hz, C3), 70.0 (^1J(CH) 125 Hz, C2), 110.0, 113.2, 113.4, 113.8, 114.4, 116.3, 117.3, 122.4, 126.1 (R-C_5H_4), 124.0, 124.3, 124.5, 133.2, 153.8, 194.7 (arom. C) ppm.

Thermolysis of bis(η-t-butylcyclopentadienyl)diphenyltitan

(a) In a sealed 5 mm NMR tube a 10% solution of $(Me_3C\text{-}Cp)_2TiPh_2$ (**1c**) in 0.5 mL of benzene-d_6 was heated at 80–85 ° C. NMR monitoring revealed than the reaction was complete after ca. 2 h. The products **5a** and benzene were identified from their ^{1}H/^{13}C NMR spectra (see below).

(b) For the polymerization experiments a solution of 0.05 g (0.113 mmol) of **1c** in 5 mL of toluene was heated in a sealed Schlenk-tube for 2 h at 85 ° C; then an aliquot was stripped *in vacuo* and analyzed by means of ^{1}H NMR spectroscopy, which revealed that the C–H activation product **5a** was formed, accompanied by ca. 10% of an additional, unidentified, organometallic species. The remaining toluene solution was used directly for generating the polymerization catalyst. **5a**: ^{1}H NMR (benzene-d_6): δ -1.94 and -0.08 (AB system, ^2J 10.5 Hz, 2H, CH_2), 1.03 (s, 9H, t-butyl), 1.06 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 4.63, 5.09, 5.12, 5.51, 5.87, 5.97, 6.34, 6.83 (m, each 1H, R-C_5H_4), 6.65, 6.92–7.02 (m, 5H, phenyl) ppm. ^{13}C NMR (benzene-d_6): δ 28.9 (CH_3), 29.5 (CH_3), 31.5 and 32.2 (t-butyl), 34.0 (quart. C), 57.6 (^1J(CH) 134 Hz, CH_2), 105.7, 108.3, 112.0. 112.5, 131.1, 115.7, 116.4, 118.4, 119.1, 139.2 (2 R-C_5H_4), 123.6, 126.6, 135.0, 190.0 (phenyl-C) ppm.

Thermolysis of (η-t-butylcyclopentadienyl)(η-cyclopentadienyl)diphenyltitan

(a) In a sealed NMR tube a solution (ca. 10%) of (Me_3C-Cp)CpTiPh$_2$ (**1d**) in 0.5 mL of benzene-d_6 was heated at 80–85 ° C. The ^{1}H NMR spectrum after 1.5 h revealed the presence of a **1d**/**5b** mixture of ca. 30/70. After 2 h the reaction was complete. Benzene was observed as a reaction product.

(b) For the polymerization reactions a solution of **5b** was prepared by heating 0.55 g (1.4 mmol) of **1d** in 20 mL of heptane for 2 h at 80–85 ° C. The product was characterized by NMR spectroscopy on an aliquot of the solution. For the polymerization experiments the heptane solution of **5b** was used without further purification. **5b**: ^{1}H NMR (benzene-d_6): δ -2.25 and 0.06 (AB system, ^2J 10.3 Hz, 2H, CH_2), 0.98 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 4.55, 4.89, 5.86, 6.77 (m, 1H each, R-C_5H_4), 5.72 (s, 5H, Cp), 6.41 (m, 2H), 6.90–7.10 (m, 3H, phenyl). ^{13}C NMR (benzene-d_6): δ 29.08 (CH_3), 29.14 (CH_3), 34.4 (quart. C), 57.6 (CH_2), 105.5, 111.2, 114.6, 119.1, 119.5 (R-C_5H_4), 113.3 (Cp), 123.3, 127.2, 133.4, 190.8 (phenyl-C) ppm.

Propene polymerization reactions

These were carried out in a two-necked Schlenk tube (500 mL) immersed in a thermostated cooling bath. The tube was charged with the methylalumoxane (see Table 5) and toluene (ca. 200 mL) was added. At -60 ° C ca. 70 mL of propene was condensed into the solution. The mixture was then allowed to warm to the chosen reaction temperature. When thermal equilibration was complete, the titanocene catalyst component was added and the polymerization reaction allowed to proceed for the period indicated in Table 5. The mixture was then added to a mixture of 20 mL of concentrated aqueous HCl and 800 mL of methanol. The polymer was separated from the solution and washed twice with 200 mL of methanol, then dried *in vacuo* at 40 ° C. The results of the polymer characterization are given in Table 5.

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