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New indenyl titanium catalysts for syndiospecific styrene polymerizations☆

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Abstract

A series of multi-methyl-substituted indenes as well as allylindene, *n*-propylindene, *n*-but-1-enylindene, and *n*-butylindene have been prepared in good yields. The substituted indenes were converted into trimethylsilyl derivatives via reactions of intermediate organolithium complexes with chlorotrimethylsilane. The corresponding titanium complexes were synthesized in excellent yields from reactions of the trimethylsilyl derivatives with $TiCl_4$. The titanium complexes were evaluated as styrene polymerization catalysts in toluene solution when activated by methylaluminoxane. In general, catalytic activities decreased with each additional methyl substituent. Syndiospecificities were very high (90–95%).

Keywords: Titanium; Lithium; Ion-pairs; Indenyl complexes; Styrene; Polymerization

1. Introduction

η^5-(Cyclopentadienyl)trichlorotitanium ($CpTiCl_3$) and its analogs have been demonstrated to be effective syndiospecific catalyst precursors for the Ziegler–Natta polymerization of styrene when activated by methylaluminoxane (MAO) [1]. Several studies have demonstrated that substitution of the η^5-cyclopentadienyl or η^5-indenyl ligands in metallocene and *ansa*-metallocene Ziegler–Natta catalysts can influence both the catalyst activity and polymer stereoregularity [2]. We have previously reported [3] that replacing the cyclopentadienyl ligand with an indenyl (Ind) ligand increases the catalytic activity, stereospecificity, and thermal stability of the catalyst at elevated temperatures, and that electron-releasing substituents on the indenyl ligand can increase catalytic activity and in general increase syndiospecificity. On the other hand, bulky substituents or Lewis base groups on the indenyl ligand were found to reduce catalytic activity dramatically.

In order to further investigate these effects, we have synthesized a series of multi-methyl-substituted indenyltrichlorotitanium complexes and compared their relative catalytic activities toward styrene when activated with MAO.

2. Results and discussion

2.1. Synthesis of catalyst precursors

2.1.1. Synthesis of multi-methylated indenes

Indenes with more than one methyl group were synthesized from the corresponding highly methylated indanones using modifications of literature procedures [4]. The highly methylated indanones were prepared by reactions of the appropriate combination of acid chloride (acryloyl chloride, crotonoyl chloride, or tigloyl chloride) and either benzene or methyl-substituted benzenes (*p*-xylene or 1,2,3,4-tetramethylbenzene) in the presence of $AlCl_3$ (Eq. 1).

☆ Dedicated to Professor Alberto Ceccon on his 65th birthday in recognition of his outstanding contributions to Organometallic Chemistry.

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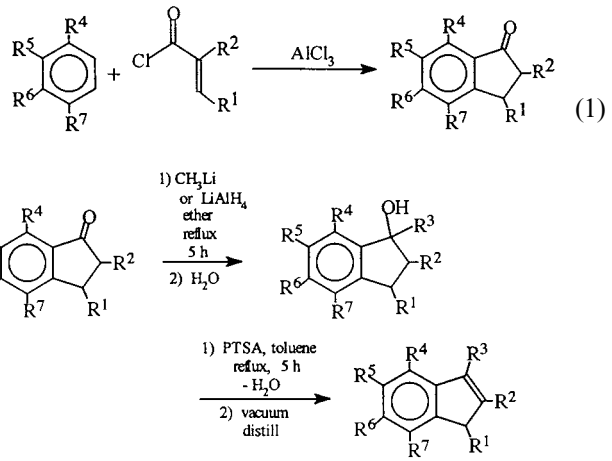
The highly methylated indanones were converted to indanols either by reaction with methyllithium or by reduction using $LiAlH_4$ followed by hydrolysis. The indanols were then dehydrated using *p*-toluenesulfonic acid in refluxing toluene to produce the desired multi-methylated indenes (**I**–**VII**, Eq. 2).



(1)

I: $R^{1,2} = CH_3$; $R^{3-7} = H$

II: $R^{1,3} = CH_3$; $R^{2,4-7} = H$

III: $R^{1-3} = CH_3$; $R^{4-7} = H$

IV: $R^{1,3,4,7} = CH_3$; $R^{2,5,6} = H$

V: $R^{4-7} = CH_3$; $R^{1-3} = H$

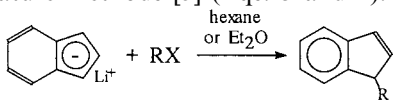
VI: $R^{2-7} = CH_3$; $R^{1} = H$

VII: $R^{1-7} = CH_3$

(2)

2.1.2. Synthesis of mono alkyl-substituted indenes

Mono-alkylindenes substituted at the 1- or 3-position were synthesized via reactions of indenyllithium with alkyl or alkenyl halides using hexane, ethyl ether, or tetrahydrofuran as a solvent by modifications to the literature methods [5] (Eqs. 3 and 4).

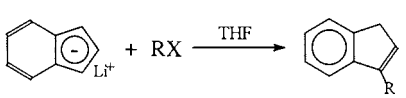


VIII: R = CH_2=$CHCH_2$

IX: R = $CH_3CH_2CH_2$

X: R = $CH_3CH_2CH_2CH_2$

(3)



XI: R = CH_2=$CHCH_2CH_2$

(4)

Substitution at the 2-position does not occur via this method probably because substitution at the less electron dense C-2 carbon [6] may require the formation of a high energy isoindene intermediate.

We reported previously [3a] that the particular solvent used in these substitution reactions controlled which isomer was isolated, consistent with the results of others [5]. When the reactions between the indenyllithium and the alkyl or alkenyl halides ($CH_3(CH_2)_2Br$, CH_2=$CHCH_2Br$, and $CH_3(CH_2)_3Br$) occured in hexane or ethyl ether solution, the 1-position alkyl or alkenyl-substituted indene isomer was isolated (Eq. 3). When this type of substitution reaction was carried out with CH_2=$CHCH_2CH_2Br$ in THF solution, the 3-position alkyl-substituted indene isomer was isolated (Eq. 4).

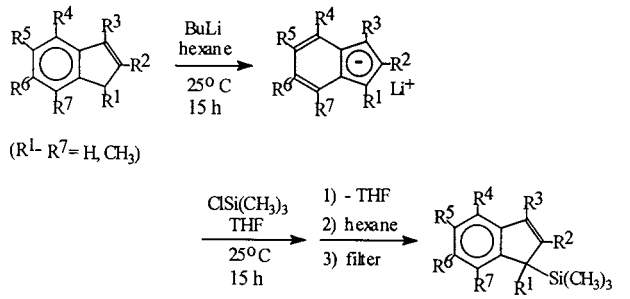
When an indenyl anion substitutes on an organic substrate, the 1-alkylindene isomer must be formed initially. The question that arises is, why do these substitution reactions lead via tautomerization to the 3-alkylindene isomer in THF but not to any appreciable extent in ethyl ether or hexane?

Several explanations are possible for the isomerization of 1-alkylindenes to 3-alkylindenes in THF but not in ethyl ether or hexane. They are the result of solvent stabilization of the transition state ion-pair [7].

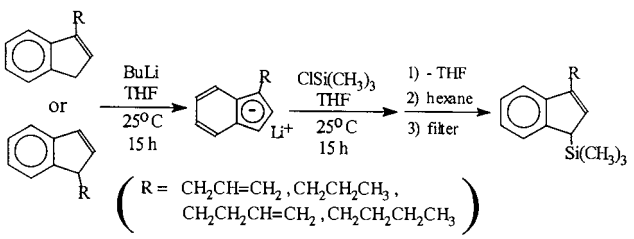
In THF, the indenyl–lithium ion pair is apparently solvent separated to a much greater degree than the same ion pair in ethyl ether or alkane solvents [5d, 8]. The ^{1}H-NMR spectrum of indenyllithium in THF shows that the protons at the 1- and 3-positions are magnetically equivalent [9], consistent with the idea of a solvent separated ion pair. (note: the idea of a THF solvent separated ion pair is disputed [10].) Thus, once any alkyl-substituted indene is formed, another THF solvated indenyl anion can act as a base catalyst and is able to isomerize the substituted indene easily to the more thermodynamically stable 3-isomer [11]. The extended reaction times used in this process would ostensibly allow for near total conversion to the more stable isomer. In hexane or ethyl ether, however, indenyllithium forms a contact ion pair which is incapable, either due to sterics or by virtue of its substantially reduced solubility in these solvents, to act as a base. Thus, very little isomerization of the 1-alkylindene formed to 3-alkylindene occurs in these solvents.

2.1.3. Synthesis of trimethylsilylindenes

Trimethylsilylindenes were prepared in high yields via reactions of indenyllithium intermediates with chlorotrimethylsilane using modifications of literature procedures [12]. The reactions of chlorotrimethylsilane with the anions of highly methylated indenes were carried out in THF to insure completeness, since it is much more difficult to lithiate these ligands than mono-alkylated indenes (Eq. 5). Reactions of 1- or 3-alkyl substituted indenyllithium intermediates with chlorotrimethylsilane in hexane formed the corresponding 1-trimethylsilyl-3-alkylindene (Eq. 6). The formation of this isomer under these conditions is consistent with the action of strong thermodynamic driving forces: (1) the alkyl substituent prefers to be in the 3-position, stabilizing the 5-membered ring double bond; and (2) the trimethylsilyl group prefers to be in the 1-position to alleviate co-planar peri-steric interactions.



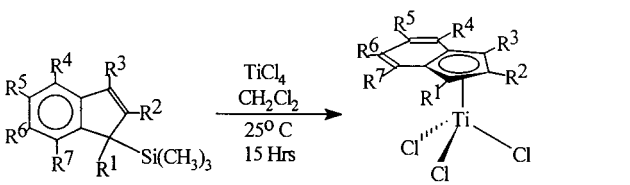
(5)



(6)

2.1.4. Synthesis of mono-indenyl titanium complexes

η^5-Indenyltrichlorotitanium complexes (**1**–**7**, **9**–**12**) were synthesized by adapting the literature procedures for the synthesis of $CpTiCl_3$ [13a] and Cp^*TiCl_3 (**8**) [13b]. The trimethylsilylindene derivatives were reacted with $TiCl_4$ in methylene chloride at ambient temperature to give the corresponding mono-indenyl titanium complexes in excellent yields (Eqs. 7 and 8). The titanium complexes in this study are appreciably more soluble in organic solvents than similar complexes synthesized previously. Hence, they were best purified by crystallization from pentane. In general, the organometallic complexes reported here decompose within 2 h in the solid state, and within an hour in solution, when they are exposed to normal atmosphere. While this work was in progress [14], the synthesis and X-ray structure for η^5-heptamethylindenyltrichlorotitanium [4f] as well as the synthesis and *s*-PS activity for 1,3-dimethylindenyltrichlorotitanium [15] were reported in the literature.



1: $R^{1,2} = CH_3$; $R^{3-7} = H$

2: $R^{1,3} = CH_3$; $R^{2,4-7} = H$

3: $R^{1-3} = CH_3$; $R^{4-7} = H$

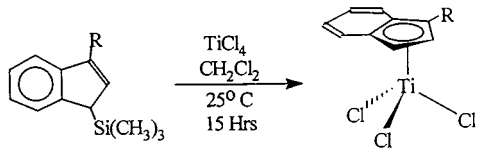
4: $R^{1,3,4,7} = CH_3$; $R^{2,5,6} = H$

5: $R^{4-7} = CH_3$; $R^{1-3} = H$

6: $R^{1,2,4-7} = CH_3$; $R^{3} = H$

7: $R^{1-7} = CH_3$

(7)



9: R = CH_2=$CHCH_2$

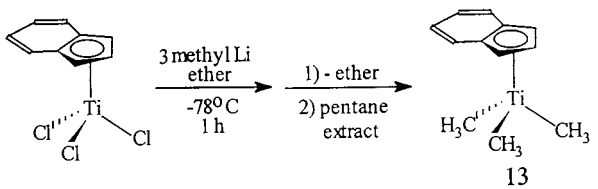
10: R = $CH_3CH_2CH_2$

11: R = CH_2=$CHCH_2CH_2$

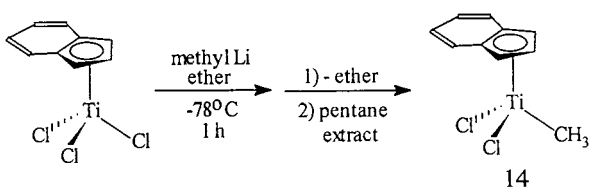
12: R = $CH_3CH_2CH_2CH_2$

(8)

It was hoped that the synthesis of indenyltrimethyltitanium (**13**) would lead to catalyst precursors which could be activated with trityl tetrakis-(pentafluorophenyl)borate [16]. Indenyltrimethyltitanium was synthesized via reaction of indenyltrichlorotitanium with three equivalents of methyllithium (Eq. 9). Although a suitable ^{1}H-NMR spectrum of (**13**) was obtained, a complementary analytical analysis was not obtained due to the thermal instability of the compound. A sequential methylation of $IndTiCl_3$ was also tried, and indenyldichloromethyltitanium (**14**) was successfully isolated (Eq. 10). However, attempts to convert **14** to higher methylated analogues failed.

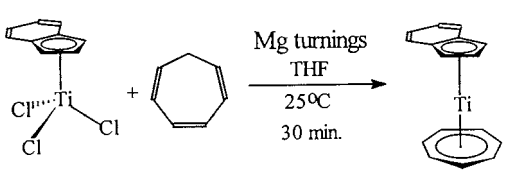


(9)



(10)

The mixed ring complex η^5-indenyl-η^7-cycloheptatrienyltitanium (**15**) was synthesized by reacting $IndTiCl_3$ with Mg turnings in the presence of cycloheptatriene under modified literature conditions previously described [17] for $CpTi(C_7H_7)$ (Eq. 11).



(11)

2.2. Polymerization results

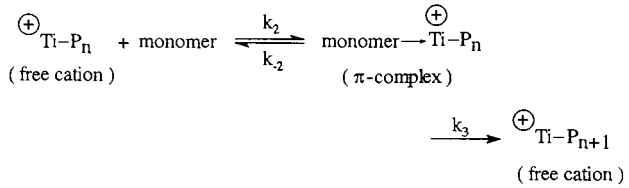
Our previous study [3a] indicated that differences in activities between the catalysts containing the same

ancillary ligands are, by and large, not attributable to differences in their ability to be activated by MAO solution. Thus, preactivation or aging of catalysts was not performed in this work.

Comparative polymerization results at 50, 75, and 100°C for Cp^*TiCl_3 (**8**) and the various indenyl titanium catalysts are reported in Table 1. Plots of log(styrene activity) versus T_p^{-1} for the various catalysts are shown in Figs. 1, 2 and 3.

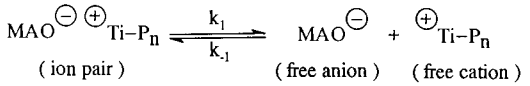
It is not a straightforward matter to compare the catalytic activities (A) of the activated Ti precursors studied in this work due to the complexity of the system involved.

Cossee and Arlman [18] proposed a mechanism in which the increasing strength of the metal/monomer π-complex enhances catalyst activity (Eq. 12). Studies using substituted styrene monomers [19] are consistent with this idea, and thus Zambelli et al. [1q–s] have postulated that the electrophilicity of the metal center is a key feature in styrene catalyst activity.



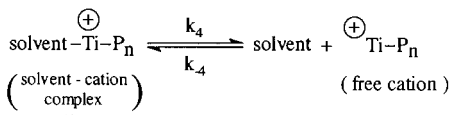
(12)

In addition, the degree of catalyst ion-pairing as analyzed by Chien and Tsai [20] was shown to be an important factor influencing polymerization activity for metallocene catalysts (Eq. 13). Pellechia et al. [16h–l] showed that replacing Cp ligand with the more electron releasing Cp* ligand in half-zirconocene catalysts greatly affected both the degree of ion-pairing and the resulting PE activities. For the polystyryl-sodium ion-pair in THF, the propagation rate constant for the free cation was shown to be two or more orders of magnitude greater than for the ion-pair [21].



(13)

Both Zambelli et al. [1r] and the Baird group [16m–n] have obtained data which show that the degree of solvent/half-metallocene association also influences catalyst activity. This can be described according to Eq. 14.



(14)

To complicate matters even more, complexes possessing several oxidation states have been shown to be active for *s*-PS [16e–f, 22]. The rate of catalyst reduction can also be influenced by η^5-ligand substitution [23].

XPS studies [24] suggest that the electron binding energy on the titanium center could be lowered by as much as 0.1 eV per methyl substituent on the η^5-ring of the cyclopentadienyl ligand and that much again by the presence of the fused benzo-ring of the indenyl ligand. One might expect methyl substitution on η^5-indenyl ligands would be a significant influence on the Ti center electrophilicity.

However, interpreting the polymerization results in terms of electrophilicity alone leads to a dichotomy between competing phenomena. On the one hand, a relatively low electron density on the metal center should enhance the electrophilicity of the catalyst, strengthening the metal/monomer π-complex (which might be expected to increase activity), as well as the degree of association within both the catalyst ion-pair and the catalyst-solvent complex (both of which might be expected to decrease activity). On the other hand, increasing electron density on the metal center (via electron releasing η^5-ligand substitution) should decrease the electrophilicity of the metal center, weakening the metal/monomer π-complex (which might be expected to decrease activity), as well as the degree of association within both the catalyst ion-pair and the catalyst–solvent complex (both of which might be expected to increase activity). Hence, determining the controlling influences on these system phenomena under various conditions presents a challenge.

In conjuction with our previous results [3], the above results show that catalytic activity for methyl-substituted $IndTiCl_3$ complexes reach a maximum with a single methyl-substitution on the η^5-indenyl ligand and, in general, decreases with additional methyl-substitutions on the indenyl ligand.

The plot of log(styrene activity) versus T_p^{-1} for $CpTi(OBu)_3$ and other half-metallocenes from previous studies [1p, 3], are convex shaped with a maxima at $T_p = 50$°C. Similar results were obtained in the present study for styrene polymerizations using **9**–**12** (Fig. 1). The effect of T_p is most pronounced for 1-(Pr)$IndTiCl_3$ (**10**), and almost imperceptible with 1-(4′-butenyl)-$IndTiCl_3$ (**11**). The styrene polymerization behaviours of ten other $IndTiCl_3$ complexes were studied and the results plotted in Figs. 2 and 3. There are three types: (A) increases with T_p^{-1}; (A) decreases with T_p^{-1}; and (A) is almost independent of T_p^{-1}. These results probably reflect different regions of the overall convex dependency seen in Fig. 1. The biggest difference in (A) is 30-fold due to a combination of steric and electronic effects.

Chien and Tsai [20] analyzed the convex dependency of effect of polymerization activity for metallocene catalysts on T_p in terms of the equilibria outlined in 12 and 13 and found an analytical solution which showed two T_p domains. At low T_p both the ion-pair and

Table 1
Styrene polymerizations using precursors activated with MAO[a]

Precursor [b]	T_p (°C)	Total yield (g)	A [c] ($\times 10^{-7}$)	s-PS [d] (%)	T_m [e] (°C)
(**1**) 1,2-$(Me)_2$IndTiCl_3	50	0.730	1.3	90.6	261.1, 271.1
	75	0.449	0.82	90.3	
	100	0.258	0.47	88.8	
(**2**) 1,3-$(Me)_2$IndTiCl_3	50	0.679	1.2	92.1	260.2, 270.6
	75	0.400	0.73	92.2	
	100	0.234	0.43	90.6	
(**3**) 1,2,3-$(Me)_3$IndTiCl_3	50	0.070	0.13	93.3	262.5, 271.2
	75	0.188	0.35	95.7	
	100	0.279	0.51	91.1	
(**4**) 1,3,4,7-$(Me)_4$IndTiCl_3	50	0.046	0.084	92.3	261.1, 271.5
	75	0.115	0.21	93.7	
	100	0.118	0.35	90.0	
(**5**) 4,5,6,7-$(Me)_4$IndTiCl_3	50	0.240	0.44	95.4	261.2, 271.6
	75	0.465	0.85	94.1	
	100	0.494	0.90	87.0	
(**6**) 1,2,4,5,6,7-$(Me)_6$IndTiCl_3	50	0.0219	0.040	89.9	261.0, 270.2
	75	0.036	0.066	87.4	
	100	0.050	0.092	86.4	
(**7**) 1,2,3,4,5,6,7-$(Me)_7$IndTiCl_3	50	0.105	0.19	94.7	262.5, 271.7
	75	0.132	0.24	92.5	
	100	0.195	0.35	91.5	
(**8**) Cp*TiCl_3	50	0.029	0.052	95.1	262.2, 271.5
	75	0.054	0.13	92.3	
	100	0.068	0.13	89.4	
(**9**) 1-(Allyl)IndTiCl_3	0	0.036	0.067	76.0	
	25	0.119	0.22	75.2	
	50	0.255	0.47	77.5	260.8, 270.6
	75	0.231	0.42	71.4	
	100	0.227	0.42	73.5	
(**10**) 1-(Pr)IndTiCl_3	0	0.019	0.036	80.3	
	25	0.389	0.72	81.7	
	50	1.051	1.9	82.1	260.3, 268.1
	75	0.482	0.84	77.8	
	100	0.425	0.78	72.8	
(**11**) 1-(Butenyl)IndTiCl_3	0	0.297	0.55	66.6	
	25	0.227	0.42	64.0	
	50	0.359	0.66	75.3	260.2, 271.2
	75	0.262	0.48	67.9	
	100	0.188	0.35	63.3	
(**12**) 1-(n-Bu)IndTiCl_3	0	0.022	0.040	65.3	
	25	0.051	0.094	67.8	
	50	0.130	0.24	79.6	261.2, 271.2
	75	0.085	0.16	75.6	
	100	0.084	0.15	66.6	
(**14**) Ind$TiCl_2CH_3$	50	2.055	3.8	97.7	262.2, 270.2
	75	1.046	1.9	97.7	
	100	0.827	1.5	87.7	
(**15**) IndTiCHT	50	0.070	0.13	42.5	260.2, 268.2
	75	0.035	0.064	36.0	
	100	0.003	0.0055	–	

[a] Polymerization conditions: [Ti], 50 μM; [Al]/[Ti], 4000; reaction time, 0.5 h; [styrene], 0.87 M.
[b] Cp*, η^5-pentamethylcyclopentadienyl; Ind, η^5-indenyl; Me, methyl; Pr, propyl; Bu, butyl; CHT, η^7-cycloheptatrienyl.
[c] A (activity) = (g bulk polymer)/(mol Ti)(mol monomer)(h).
[d] % s-PS = [(g of 2-butanone insoluble polymer)/(g of bulk polymer)] × 100.
[e] T_m, melting temperature of s-PS.

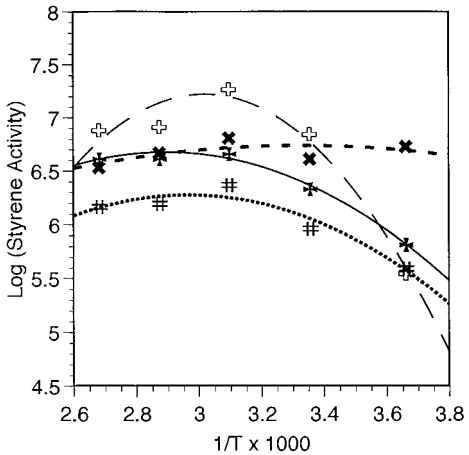


Fig. 1. Plot of log(styrene polymerization activity) versus $1/T_p \times 1000$. ✠, (**9**) 1-(allyl)-IndTiCl$_3$; ✣ (**10**) 1-(Pr)IndTiCl$_3$; **X**, (**11**) 1-(4′-But-1′-enyl)IndTiCl$_3$; #, (**12**) 1-(*n*-bu)-IndTiCl$_3$.

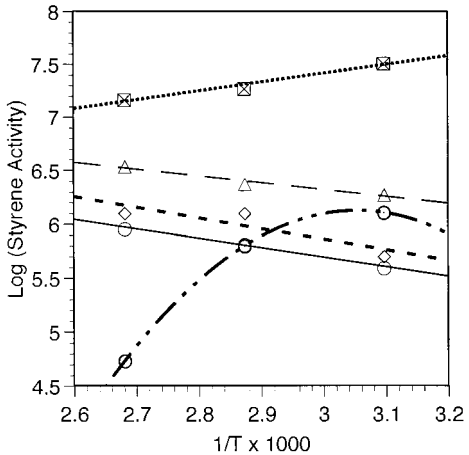


Fig. 3. Plot of log(styrene polymerization activity) versus $1/T_p \times 1000$. ○, (**6**) 1,2,4,5,6,7-(Me)$_6$-IndTiCl$_3$; △, (**7**) 1,2,3,4,5,6,7-(Me)$_7$-IndTiCl$_3$; ◇, (**8**) Cp*TiCl$_3$; ⊠, (**14**) IndTiCl$_2$CH$_3$; ⊙, (**15**) Ind-Ti(C$_7$C$_7$).

π-complex are stable and (A) is small. Increasing T_p promotes ion-pair dissociation (13) and k_3 (12) with consequent increase of (A). At high T_p, the π-complex dissociates, (A) declines, and deactivation occurs via the reduction of Ti^+(IV) species to Ti(III) products [25].

IndTi(CH$_3$)Cl$_2$ (**14**), used in conjunction with trityl-tetrakis-(pentafluorophenyl)borate co-catalyst was inactive toward styrene, presumably due to the inability of the coordinated monomer to migratory insert with another alkyl ligand. The instability of IndTi(CH$_3$)$_3$ (**13**) precluded reproducible polymerization data as well and so they are not reported.

η^5-Indenyl-η^7-cycloheptatrienyltitanium (**15**) demonstrated a very low activity toward styrene. This is probably the result of slow activation of the precursor due the difficulty in dislodging a multi-hapto ligand during alkylation [1q, 25a,c,h].

The styrene stereoselectivities of the indenyl catalysts were high, although those for catalysts with bulky substituents (**9**–**12**) were more moderate. The styrene stereoselectivity for IndTiCHT was very low. Styrene stereoselectivity of all of the catalysts decreased at 100°C as compared to 50°C and half of the catalysts show some loss of stereospecificity at 75°C.

MAO activated ethylene polymerization results for catalysts with η^5-ligands containing pendant olefin substituents (**9**, **11**) and their saturated analogs (**10**, **12**) are reported in Table 2.

Catalyst precursors (**9**, **11**) equipped with η^5-ligands containing pendant olefin substituents, ostensibly, might be expected to exhibit polymerization characteristics similar to other catalysts with coordinating pendant substituents such as (Me$_2$NCH$_2$CH$_2$–)CpTiCl$_3$ [26a,b] and particularly, (C$_6$H$_5$CH$_2$CH$_2$)CpTiCl$_3$ [26c]. If so, *s*-PS activity should be suppressed and ethylene activity enhanced compared to the corresponding complexes (**10**,**12**) possessing indenyl ligands with analogous saturated pendant substituents. The steric bulk of the ligands in **9**–**12** would be expected to limit monomer coordination and/or migratory insertion processes producing very low *s*-PS activities [3a].

However, catalyst precursors **9** and **11** exhibited a very low magnitude of activity for *both* s-PS and PE. The low PE and PP activity for **9** and **11** is consistent with the low activities seen for these monomers using half-metallocenes in general, and is considerably lower than that reported for (C$_6$H$_5$CH$_2$CH$_2$)CpTiCl$_3$ [26c].

Although there are some slight differences seen in activities between **9** and **11** versus **10** and **12**, respectively, these differences fall close to the magnitude which may be expected for uncertainty in this system, and they do not always follow the expected trend.

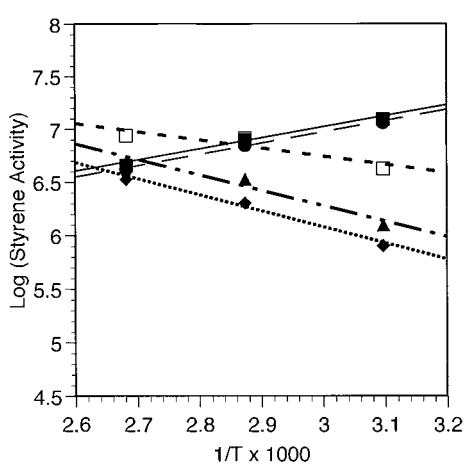


Fig. 2. Plot of log(styrene polymerization activity) versus $1/T_p \times 1000$. ■, (**1**) 1,2-(Me)$_2$IndTiCl$_3$; ●, (**2**) 1,3-(Me)$_2$IndTiCl$_3$; ▲, (**3**) 1,2,3-(Me)$_2$IndTiCl$_3$; ◆, (**4**) 1,3,4,7-(Me)$_4$IndTiCl$_3$; □, (**5**) 4,5,6,7-(Me)$_4$IndTiCl$_3$.

These results lead one to conclude that any coordination by the pendant olefin substituents in **9** and **11** is limited at best and not sufficient to promote oligomerizations of α-olefin monomers. The limited coordination (if at all) of these restricted olefins cannot compete effectively with the more powerful coordination of unrestricted arene solvents [1o,p,r] or monomers [16m–o].

3. Experimental

All operations were carried out under argon atmosphere using standard Schlenk and glove box techniques unless otherwise noted. Methylene chloride was distilled under argon from calcium hydride. All other solvents were distilled under argon form sodium–potassium alloy. $TiCl_4$ was distilled (trap to trap) from copper turnings prior to use. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. ^{1}H-NMR spectra were obtained on a Bruker NR-80 spectrometer. Melting points of the polymers were obtained using a Perkin Elmer model DSC-4 differential scanning calorimeter.

3.1. Synthesis of tigloyl chloride, crotonoyl chloride, and acryloyl chloride

In a fume hood, thionyl chloride (300 ml, 4.11 mol) and 100 g of the appropriate acid (0.998 mol tiglic acid; 1.16 mol crotonic acid; 1.16 mol, 98.5 ml, methacrylic acid; 1.39 mol, 95 ml acrylic acid) were introduced into a 500 ml round bottom flask fitted with a magnetic stirring apparatus and a reflux condenser. The mixture was refluxed for 15 h at which time the reflux condenser was replaced with a distillation head and condenser. Excess thionyl chloride was distilled at 78°C and ambient pressure, followed by the resulting acid chloride (methacryloyl chloride: 95–96°C; crotonoyl chloride: 118–125°C; tigloyl chloride: 130–140°C). In the case of acryloyl chloride, the excess thionyl chloride was removed under vacuum (25°C, 0.01 mmHg), followed by acryloyl chloride (35–40°C, 0.01 mmHg).

*3.2. Synthesis of 1,2-dimethylindene (**I**) [11o]*

Benzene (300 ml, 3.35 mol) and aluminum trichloride (80 g, 0.6 mol) were introduced into a three neck 500 ml round bottom flask fitted with a magnetic stirring apparatus, an addition funnel, and a reflux condenser. The stirred mixture was cooled to 0°C and 27 g of tigloyl chloride (0.31 mol) was added dropwise via the addition funnel. After the addition was complete, the mixture was allowed to warm to room temperature and then refluxed overnight. The mixture was cooled to room temperature and poured into a 1000 ml beaker containing 300 g of ice and 50 ml of concentrated hydrochloric acid. The organic layer was extracted three times with 100 ml portions of a saturated solution of sodium bicarbonate, then dried over anhydrous magnesium sulfate. The excess benzene was removed under reduced pressure to leave an orange oil of 2,3-dimethyl-1-indanone (41 g, 0.26 mol, 84% yield).

A diethyl ether solution (100 ml) of 2,3-dimethyl-1-indanone (20 g, 0.125 mol) was added dropwise via syringe under argon to a 500 ml side-armed round-bottomed flask containing a stirred slurry of lithium aluminum hydride (5.7 g, 0.15 mol) in 250 ml of diethyl ether, fitted with a magnetic stirring apparatus and a reflux condenser with a gas outlet valve connected to a mercury overpressure bubbler. The mixture was refluxed overnight, cooled to 0°C, and 100 ml of water was added dropwise through the top of the condenser (caution!). The organic layer was washed three times with 100 ml portions of water and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure to leave a yellow residue of 2,3-dimethyl-1-indanol (16.5 g, 0.102 mol, 82% yield).

Toluene (300 ml) was added to the indanol residue and the solution was poured into a 500 ml round-bottom flask fitted with a magnetic stirring apparatus and a Dean–Stark apparatus. A catalytic amount of *p*-toluenesulfonic acid (50 mg) was added and the solution refluxed for 5 h at which time the water layer was removed and excess toluene distilled via the Dean–Starke arm. After the mixture was cooled, the organic

Table 2
Ethylene polymerizations using precursors activated with MAO[a,b]

Temperature (°C)	Activity ($\times 10^{-4}$) (g PE/{(mol Ti)([ethylene])(h)})			
	1-(Allyl)IndTiCl$_3$ (**9**)	1-(Pr)IndTiCl$_3$ (**10**)	1-(Butenyl)IndTiCl$_3$ (**11**)	1-(Bu)IndTiCl$_3$ (**12**)
0	5.5	5.0	1.3	0.62
25	3.5	3.0	1.2	0.35
50	2.5	3.9	1.7	0.14

[a] Polymerization conditions: [Ti], 50 μM; Al/Ti, 4000, ethylene, 15 psig; total reaction volume, 50 ml; reaction time, 2 h.
[b] Ind, η^5-indenyl; Me, methyl; Pr, propyl; Bu, butyl; Butenyl, 1-4′-butenyl.

residue was washed three times with 100 ml portions of saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The dark yellow residue was distilled under vacuum (90–95°C, 0.01 mmHg) to give a pale yellow fraction of 1,2-dimethylindene (**I**, 12.1 g, 0.085 mol, 83% yield, 57% overall yield). ^{1}H-NMR: ($CDCl_3$) δ 7.4–7.05 (m, 4H, arom.), 6.41 (m, 1H, sp^2 3-position, J(3-2-position CH_3 = 0.68 Hz, J(3–1) = 0.68 Hz), 3.21 (qm, 1H, sp^3 1-position, J(1-1-position CH_3 = 8.0 Hz, J(1–3) = 0.68 Hz, J(1-2-position CH_3) = 0.68 Hz), 2.055 (dd, 3H, 2-position CH_3, J(CH_3-1) = 0.68 Hz, J(CH_3-3) = 0.68 Hz), 1.28 (d, 3H, 1-position CH_3, J(CH_3-1) = 8.0 Hz).

3.3. Synthesis of 1,3-dimethylindene (*II*)

3.3.1. Method A [11j, 27]

Benzene (300 ml, 3.35 mol) and aluminum trichloride (80 g, 0.60 mol) were introduced into to a three neck 500 ml round bottom flask fitted with a magnetic stirring apparatus, an addition funnel, and a reflux condenser. The stirred mixture was cooled to 0°C and 27 g of crotonyl chloride (19.4 ml, 21.14 g, 0.20 mol) was added dropwise via the addition funnel. After the addition was complete, the mixture was allowed to come to room temperature and then refluxed overnight. The mixture was cooled to room temperature and poured into a 1000 ml beaker containing 300 g of ice and 50 ml of concentrated hydrochloric acid. The organic layer was extracted three times with 100 ml portions of a saturated solution of sodium bicarbonate then dried over anhydrous magnesium sulfate. The excess benzene was removed under reduced pressure to leave an orange oil of 3-methyl-1-indanone (25.8 g, 0.178 mol, 88% yield).

Diethyl ether (250 ml), and 20 g, 0.138 mol of 3-methyl-1-indanone were added under argon to a 500 ml side-armed round-bottomed flask fitted with a magnetic stirring apparatus and a reflux condenser with a gas outlet valve connected to a mercury overpressure bubbler. Methyl lithium (143 ml, 1.4 M in diethyl ether, 0.20 mol) was added dropwise via syringe and the mixture was refluxed overnight. The mixture was cooled to 0°C and 100 ml of saturated amonium chloride solution was added dropwise through the top of the condenser. The organic layer was washed three times with 100 ml portions of water and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure to leave a yellow residue of 1,3-dimethyl-1-indanol (20.3 g, 0.139 mol, 78% yield).

Toluene (300 ml) was added to the indanol residue and the solution was poured into a 500 ml round-bottom flask fitted with a magnetic stirring apparatus and a Dean–Stark apparatus. A catalytic amount of *p*-toluenesulfonic acid (50 mg) was added and the solution refluxed for 5 h at which time the water layer was removed and excess toluene distilled via the Dean–Stark arm. After the mixture was cooled, the organic residue was dissolved into 100 ml of diethyl ether, washed three times with 100 ml portions of saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, and the dark yellow residue was distilled under vacuum (90–95°C, 0.01 mmHg) to give a pale yellow fraction of 1,3-dimethylindene (**II**, 15.0 g, 0.104 mol, 75% yield, 51.5% overall yield).^{1}H-NMR ($CDCl_3$): δ 7.36–7.20 (m, 4H, arom.), 6.11 (s, 1H, sp^2 2-position), 3.40 (q, 1H, sp^3 1-position, J(1-1-position CH_3) = 7.5 Hz), 2.12 (s, 3H, 3-position CH_3), 1.27 (d, 3H, 1-position CH_3, J(1-position CH_3-1) = 7.5 Hz).

3.3.2. Method B [5d, 11a]

Butyllithium (48 ml, 1.6 M in hexane, 0.077 mol) was added dropwise via a syringe to a hexane solution (150 ml) of 3-methylindene [3a] (10 g, 0.077 mol) contained in a 500 ml side-armed flask fitted with a gas outlet connected to a mercury overpressure valve. The solution was allowed to stir overnight at room temperature which produced a white precipitate of 1-methylindenyllithium. The supernatent liquid was removed using a filter cannula and replaced with 200 ml of THF. (Note: The solvation of a dry lithium salt in THF is exothermic and may require cooling.) Iodomethane (5.0 ml, 0.08 mol) was added dropwise via syringe to the THF solution containing the lithium salt and the reaction mixture allowed to stir overnight at room temperature. The THF was removed under reduced pressure and replaced with 200 ml of hexane. Butyllithium (48 ml, 1.6 M in hexane, 0.077 mol) was added dropwise via a syringe and the mixture allowed to stir overnight resulting in a white precipitate of 1,3-dimethylindenyllithium. The supernatant liquid was removed using a filter cannula and discarded. The white precipitate was washed twice with 100 ml portions of hexane which were removed using a filter cannula and discarded. Hexane (200 ml) was introduced to the lithium salt followed by the addition of 100 ml of water in small portions through the top of the flask. The hexane–water solution was vigorously stirred for 30 min after which the hexane fraction was isolated using a separatory funnel and dried over anhydrous $MgSO_4$. The hexane was removed under reduced pressure and the residue distilled under vacuum (90–95°C, 0.01 mmHg) to give a pale yellow fraction of 1,3-dimethylindene (**II**, 7.2 g, 0.055 mol, 72% yield). The ^{1}H-NMR spectrum of the product was identical to that for **II** obtained by Method A.

3.4. Synthesis of 1,2,3-trimethylindene (*III*) [4d]

Utilizing the procedure for 1,3-dimethylindene (Method A), 2,3-dimethyl-1-indanone was prepared in 84% yield (41 g) from benzene (300 ml, 3.35 mol),

aluminum trichloride (80 g, 0.6 mol) and tigloyl chloride (27 g, 0.31 mol). A subsequent reaction of 2,3-dimethyl-1-indanone (15.0g, 0.0938 mol) in 250 ml of diethyl ether with methyl lithium (71 ml, 1.4 M in diethyl ether, 0.10 mol) followed by hydrolysis afforded 1,2,3-trimethyl-1-indanol in 86% yield (14.2 g) as a yellow residue. Dehydration of the indanol residue in 300 ml of toluene containing 50 mg of *p*-toluenesulfonic acid followed by distillation (92–98°C, 0.01 mmHg) gave a pale yellow fraction of 1,2,3-trimethylindene (**III**, 10.05 g, 0.0635 mol, 79% yield, 57.1% overall yield based on tigloyl chloride). ^{1}H-NMR: ($CDCl_3$) δ 7.53–7.0 (m, 4H, arom.), 3.17 (q, 1H, sp^3 1-position, J(1-1-position CH_3) = 7.44 Hz), 2.02 (q, 3H, 2-position CH_3, J(2-position CH_3-3-position CH_3) = 0.96 Hz), 1.97 (q, 3H, 3-position CH_3, J(3-position CH_3-2-position CH_3 = 0.96 Hz), 1.30 (d, 3H, 1-position CH_3, J(1-position CH_3-1) = 7.44 Hz).

3.5. Synthesis of 1,3,4,7-tetramethylindene (IV)

The method of preparation was the same as for 1,3-dimethylindene (Method A) except that *p*-xylene (200 ml, 1.63 mol) and aluminum trichloride (26.7 g, 0.2 mol) were used in conjunction with 10 g of crotonyl chloride (0.096 mol) to produce 14.5 g (87.5% yield) of 3,4,7-trimethyl-1-indanone as an orange oil. The indanone was in turn reacted with methyl lithium (64.3 ml, 1.4 M in diethyl ether, 0.09 mol) and the subsequent work-up produced a yellow residue of 1,3,4,7-tetramethyl-1-indanol (13 g, 82% yield). Dehydration and work-up of the indanol produced a dark yellow residue, which was distilled under vacuum (92–98°C, 0.01 mmHg) to give a pale yellow fraction of 1,3,4,7-tetramethylindene (**IV**, 9.2 g, 78% yield, 56% overall yield). ^{1}H-NMR: ($CDCl_3$) δ 6.68 (m, 2H, arom.), 6.05 (m, 1H, sp^2 2-position, J(2-1) = 1.92 Hz, J(2-3-position CH_3) = 1.68 Hz), 3.38 (qm, 1H, sp^3 1-position, J(1-1-position CH_3) = 7.28 Hz, J(1-2) = 1.92 Hz, J(1-3-positon CH_3) = 1.68 Hz), 2.53 (s, 3H, 4-position CH_3), 2.36 (s, 3H, 7-position CH_3), 2.29 (dd, 3H, 3-position CH_3, J(3-position CH_3-1) = 1.68 Hz, J(3-position CH_3-2) = 1.68 Hz), 1.24 (d, 3H, 1-position CH_3, J(1-position CH_3-1) = 7.28 Hz).

3.6. Synthesis of 4,5,6,7-tetramethylindene (V)

The method of preparation was the same as for 1,2-dimethylindene except that 1,2,3,4-tetramethylbenzene (200 ml, 1.33 mol) and aluminum trichloride (29 g, 0.22 mol) were used in conjuction with 10 g of acryloyl chloride (0.111 mol) to produce an orange oil of 4,5,6,7-tetramethyl-1-indanone (18.8 g, 90% yield). The indanone was in turn reacted with lithium aluminum hydride (4.5 g, 0.12 mol), which upon work-up produced a yellow residue of 4,5,6,7-tetramethyl-1-indanol (15.6 g, 82% yield). Dehydration and work-up of the indanol produced a dark yellow residue, which was distilled under vacuum (90–95°C, 0.01 mmHg) to give a pale yellow fraction of 11.36 g of 4,5,6,7-tetramethylindene (**V**, 81% yield, 60% overall yield). ^{1}H-NMR: ($CDCl_3$) δ 7.00 (dt, 1H, sp^2 3-position, J(3-2) = 5.62 Hz, J(3-1) = 2.00 Hz), 6.47 (dt, 1H, sp^2 2-position, J(2-3) = 5.62 Hz, J(2-1) = 1.90 Hz), 3.33 (unresolved dd, 2H, sp^3 1-position, J(1-3) = 2.00 Hz, J(1-2) = 1.90 Hz), 2.38 (s, 3H, 4-positon CH_3), 2.30 (s, 3H, 7-position CH_3), 2.26 (s, 3H, 6-position CH_3), 2.20 (m, 3H, 5-position CH_3).

3.7. Synthesis of 2,3,4,5,6,7-hexamethylindene (VI)

The method of preparation is the same as for 1,2-dimethylindene except that 1,2,3,4-tetramethylbenzene (300 ml, 1.99 mol) and aluminum trichloride (56 g, 0.42 mol) were used in conjuction with 25 g of tigloyl chloride (0.21 mol) to produce an orange oil of 2,3,4,5,6,7-hexamethyl-1-indanone (58.3 g, 87% yield). The indanone (15 g, 0.065 mol) was in turn reacted with lithium aluminum hydride (3.00 g, 0.0791 mol), which upon work-up produced a yellow residue of 2,3,4,5,6,7-hexamethyl-1-indanol (12.6 g, 89% yield). Dehydration and subsequent work-up of the indanol produced 9.02 g of crude 1,2,4,5,6,7-hexamethylindene (this isomer is assumed based on the starting materials) as a yellow oil 78, 60% overall yield). Purification of the crude 1,2,4,5,6,7-hexamethylindene by vacuum distillation (220–225°C, 0.01 mmHg) resulted in isomerization to 2,3,4,5,6,7-hexamethylindene (**VI**), collected as a pale yellow oil which solidified on cooling. ^{1}H-NMR: ($CDCl_3$) δ 3.11 (s, 2H, sp^3 1-position), 2.49 (s, 3H, 4-position CH_3), 2.30 (s, 3H, 7-position CH_3), 2.23 (s, 6H, overlapping 5 and 6-position CH_3), 2.21 (s, 3H, 2-position CH_3), 2.02 (s, 3H, 3-position CH_3).

3.8. Synthesis of 1,2,3,4,5,6,7-heptamethylindene (VII) [4c–f]

The method of preparation was the same as for 1,3-dimethylindene (Method A) except that 1,2,3,4-tetramethylbenzene (300 ml, 1.99 mol) and aluminum trichloride (56 g, 0.42 mol) were used in conjunction with 25 g of tigloyl chloride (0.21 mol) to produce an orange oil of 2,3,4,5,6,7-hexamethyl-1-indanone (58.3 g, 87% yield). The indanone (15 g, 0.065 mol) was in turn reacted with methyl lithium (50.0 ml, 1.4 M in diethyl ether, 0.07 mol), which after work-up produced a yellow residue of 1,2,3,4,5,6,7-heptamethyl-1-indanol (11.67 g, 84% yield). Dehydration and subsequent work-up of the indanol produced a dark yellow residue of crude 1,2,3,4,5,6,7-heptamethylindene as a yellow oil (**VII**, 9.22 g, 79% yield, 58% overall yield). The crude heptamethylindene was recrystallized from methanol to

give a pale yellow powder. ^{1}H-NMR: ($CDCl_3$) δ 3.15 (q, 1H, sp^3 1-position, J(1-1-position CH_3) = 2.8 Hz), 2.48 (s, 3H, 4-position CH_3), 2.30 (s, 3H, 7-position CH_3), 2.22 (bs, 9H, overlapping 2, 5, and 6-position CH_3), 1.93 (s, 3H, 3-position CH_3), 1.21 (d, 3H, 1-position CH_3, J(1-position CH_3-1) = 2.8 Hz).

3.9. Synthesis of 1-allylindene (*VIII*)

A suspension of 10.0 g (0.082 mol) of indenyllithium in 250 ml of hexane contained in a 500 ml side-armed flask fitted with an overpressure bubbler was chilled to 0°C. 3-Chloropropene (also called allyl chloride, 6.7 ml, 0.082 mol) was added dropwise via syringe to the flask and the mixture allowed to stir overnight at room temperature. The solution was filtered through a Celite plug and the hexane removed under vacuum to yield 4.26 g (68%) of a yellow oil. The product was distilled at 62–65°C/0.001 mmHg and a colorless oil was obtained which turned yellow on standing at room temperature. ^{1}H-NMR ($CDCl_3$): δ 7.61–7.00 (m, 4H, arom.), 6.80 (dd, 1H, sp^2 3-position, J(3-2) = 5.6 Hz, J(3-1) = 1.5 Hz), 6.51 (dd, 1H, sp^2 2-position, J(2-3) = 5.6 Hz, J(2-1) = 1.7 Hz), 6.23–5.60 (complex m, 1H, sp^2 $-CH_2-$**C**$\mathbf{H}$=CH_2, J(2′-1′*trans*) = 7.0 Hz, J(2′-CH_2) = 6.7 Hz), 5.22 (d of m, 1H, sp^2, $-CH_2-CH$=C$\mathbf{H}_2$ *trans*, J(1′*trans*-2′) = 7.2 Hz, J(1′-1′) = 1.0 Hz), 4.96 (m, 1H, sp^2, $-CH_2-CH$=C$\mathbf{H}_2$ *cis*, J(1′-1′*gem*) = 1.0 Hz), 3.46 (m, 1H, sp^3 1-position, J(1-CH_2) = 7.2 Hz, J(1-2) = 1.7 Hz, J(1-3) = 1.5 Hz), 2.47 (complex m, 2H, sp^3, $-C\mathbf{H}_2-CH$=CH_2, J(CH_2-1) = 7.2 Hz, J(CH_2-2′ = 6.7 Hz).

3.10. Synthesis of 1-n-propylindene (*IX*) [5c,d]

The method of preparation was the same as for 1-allylindene except that 10.0 g (0.082 mol) of indenyllithium was reacted with 1-chloropropane (7.4 ml, 0.082 mol) to yield 9.1 g (72%) of a yellow oil. The product was distilled at 71–72°C/0.001 mmHg and a colorless oil was obtained which turned yellow on standing at room temperature. ^{1}H-NMR ($CDCl_3$): δ 7.38 (m, 2H, arom.), 7.23 (m, 2H, arom.), 6.78 (d, 1H, sp^2 3-position, J(3-2) = 5.52 Hz), 6.52 (d, 1H, sp^2 2-position, J(2-3) = 5.52 Hz), 3.45 (m, 1H, sp^3 1-position, J(1-1′) = 4.2 Hz, J(1-2) = 1.8 Hz, J(1-3) = 1.8 Hz), 1.86 (m, 2H, $-C\mathbf{H}_2CH_2CH_3$, J(1′-1) = 4.2 Hz, J(1′-2′) = 2.2 Hz), 1.46 (m, 2H, $-CH_2C\mathbf{H}_2CH_3$, J(2′-1′) = 2.2 Hz, J(2′-3′) = 3.2 Hz), 0.96 (t, 3H, $-CH_2CH_2C\mathbf{H}_3$, J(3′-2′) = 3.2 Hz).

3.11. Synthesis of 3-(4′-n-but-1′-enyl)indene (*XI*)

THF (250 ml) was added to 5.0 g (0.041 mol) of indenyllithium in a 500 ml side-armed flask fitted with an overpressure bubbler and previously chilled to 0°C. 4-Bromo-1-butene (4.2 ml, 0.041 mol) was added to the flask dropwise via a syringe maintaining the temperature at 0°C. After the addition was completed, the mixture was allowed to warm to room temperature and stirred overnight. The THF was removed under vacuum and replaced with 100 ml of hexane. The solution was passed through a silica gel column and a bright yellow band was collected. The hexane was removed under vacuum to yield 5.7 g (81%) of a yellow oil. This residue was distilled at 75–76°C/0.001 mmHg to give a colorless oil which turned yellow on standing at room temperature.^{1}H-NMR ($CDCl_3$): δ 7.4–7.2 (m, 4H, arom.), 6.22 (bs, 1H, sp^2 2-position), 5.95 (m, 1H, $-CH_2CH_2C\mathbf{H}$=CH_2, J(2′-1′*trans*) = 8.2 Hz), 5.12 (d of m, 1H, $-CH_2CH_2CH$=C$\mathbf{H}$H *trans*, J(1′*trans*-2′) = 8.2 Hz, J(1′-1′*gem*) = 0.9 Hz), 4.95 (m, 1H, $-CH_2CH_2CH$=C$\mathbf{H}$H *cis*, J(1′-1′) = 0.9 Hz), 3.32 (t of m, 2H, sp^3 1-position, J(1′-4′) = 1.4 Hz, 2.8–2.4 (m of m, 4H, $-C\mathbf{H}_2C\mathbf{H}_2CH$=$CH_2$, overlapping signals, J(4′-1′) = 1.4 Hz).

3.12. Synthesis of 1-n-Butylindene (*X*) [5c]

The method of preparation was the same as for 1-allylindene except that 10.0 g (0.082 mol) of indenyllithium was reacted with 1-bromobutane (9.0 ml, 0.082 mol) producing a yellow oil. The product was distilled at 75–76°C/0.001 mmHg and a colorless oil was obtained which turned yellow on standing at room temperature. ^{1}H-NMR ($CDCl_3$): δ 7.38 (m, 2H, arom.), 7.23 (m, 2H, arom.), 6.78 (d, 1H, sp^2 3-position, J(3-2) = 5.52 Hz), 6.52 (d, 1H, sp^2 2-position, J(2-3) = 5.52 Hz), 3.45 (m, 1H, sp^3 1-position, J(1-1′) = 4.2 Hz), 1.86 (m, 2H, $-C\mathbf{H}_2CH_2CH_2CH_3$, J(1′-1) = 4.2 Hz), 1.62–1.20 (m, 4H, overlapping signals $-CH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$, J(3′-4′) = 3.2 Hz), 0.96 (t, 3H, $-CH_2CH_2CH_2C\mathbf{H}_3$, J(4′-3′) = 3.2 Hz).

3.13. Synthesis of 1-trimethylsilyl-2,3-dimethylindene (*XII*)

Butyllithium (44 ml, 1.6 M in hexane, 0.07 mol) was added to a solution of 1,2-dimethylindene (**I**, 10 g, 0.069 mol) in 100 ml of THF contained in a magnetically stirred 200 ml side-armed round-bottomed flask fitted with a gas-outlet valve connected to a mercury overpressure valve. After the solution had stirred for 4 h, chlorotrimethylsilane (10.2 ml, 0.08 mol) was added to the flask via a syringe and stirring was continued overnight. The THF and excess chlorotrimethylsilane were removed under reduced pressure, replaced with 100 ml of dry hexane, and stirred for 15 min. The hexane solution was filtered using a filter cannula and the solvent was removed under reduced pressure to yield 1-trimethylsilyl,2,3-dimethylindene as a yellow oil (11.6 g, 0.053 mol, 77% yield). ^{1}H-NMR: ($CDCl_3$) δ 7.45–7.15 (m, 4H, arom.), 3.34 (bs, 1H, sp^3 1-position), 2.19 (bs, 6H, overlapping 2 and 3-position CH_3), 0.05 (s, 9H, $Si(CH_3)_3$).

3.14. Synthesis of 1-trimethylsilyl-1,3-dimethylindene (XIII)

1,3-Dimethylindene (**II**, 5.0 g, 0.035 mol) was dissolved in 100 ml of hexane contained in a 250 ml side-armed flask fitted with a gas inlet connected to an overpressure bubbler. To this solution 27.1 ml of 1.6 M *n*-butyllithium (0.035 mol) was added dropwise and the mixture was stirred overnight at room temperature. The supernatant liquid was decanted and the white precipitate was washed with three 100 ml portions of hexane. Fresh hexane (100 ml) was introduced to the flask, 5.5 ml (0.043 mol) of chlorotrimethylsilane was added dropwise via a syringe to the stirred suspension, and the mixture was allowed to stir overnight. The solution was then filtered through a Celite plug and the solvent removed under vacuum, leaving 6.23 g (0.0287 mol, 82% yield) of a yellow oil. The crude product was further purified via distillation at 87–88°C/0.001 mmHg to yield a colorless oil which darkened on standing at room temperature. ^{1}H-NMR: ($CDCl_3$) δ 7.26 (m, 4H, arom.), 6.16 (d, 1H, sp^2 2-position, J(2-3-position CH_3) = 1.4 Hz), 2.18 (d, 3H, 3-position CH_3, J(CH_3-2) = 1.4 Hz), 1.42 (s, 3H, 1-position CH_3), −0.16 (s, 9H, $Si(CH_3)_3$).

3.15. Synthesis of 1-trimethylsilyl-1,2,3-trimethylindene (XIV)

The method of preparation was the same as for 1-trimethylsilyl-2,3-dimethylindene except that butyllithium (21.9 ml, 1.6 M in hexane, 0.035 mol) was reacted with 1,2,3-trimethylindene (**III**, 5.0 g, 0.032 mol), followed by reaction with chlorotrimethylsilane (5.1 ml, 0.04 mol). Work-up of the residue yielded 1-trimethylsilyl-1,2,3-trimethylindene as a yellow oil (5.15 g, 70% yield). ^{1}H-NMR: ($CDCl_3$) δ 7.44–7.22 (m, 4H, arom.), 2.19 (m, 3H, 2-position CH_3, J(2-position CH_3-3-position CH_3) = 0.91 Hz), 2.11 (m, 3H, 3-postion CH_3, J(3-position CH_3-2-position CH_3) = 0.91 Hz), 1.55 (s, 3H, 1-position CH_3), −0.04 (s, 9H, $Si(CH_3)_3$).

3.16. Synthesis of 1-trimethylsilyl-1,3,4,7-tetramethylindene (XV)

The method of preparation was the same as for 1-trimethylsilyl-2,3-dimethylindene except that butyllithium (18.8 ml, 1.6 M in hexane, 0.03 mol) was reacted with 1,3,4,7-tetramethylindene (**IV**, 5.0 g, 0.029 mol), followed by reaction with chlorotrimethylsilane (5.1 ml, 0.04 mol). Work-up of the residue yielded 1-trimethylsilyl-1,3,4,7-tetramethylindene as a yellow oil (3.58 g, 71.7% yield). ^{1}H-NMR: ($CDCl_3$) δ 6.63 (s, 2H, arom.), 6.03 (d, 1H, sp^2 2-position, J(2-3-position CH_3) = 1.20 Hz), 2.56 (s, 3H, 4-position CH_3), 2.40 (s, 3H, 7-position CH_3), 2.34 (d, 3H, 3-position CH_3, J(3-position CH_3-2) = 1.20 Hz), 1.55 (s, 3H, 1-position CH_3), −0.13 (s, 9H, $Si(CH_3)_3$).

3.17. Synthesis of 1-trimethylsilyl-4,5,6,7-tetramethylindene (XVI)

The method of preparation was the same as for 1-trimethylsilyl-2,3-dimethylindene except that butyllithium (18.8 ml, 1.6 M in hexane, 0.03 mol) was reacted with 4,5,6,7-tetramethylindene (**V**, 5.0 g, 0.029 mol), followed by reaction with chlorotrimethylsilane (5.1 ml, 0.04 mol). Work-up of the residue yielded 1-trimethylsilyl-4,5,6,7-tetramethylindene as a yellow oil (4.1 g, 82% yield). ^{1}H-NMR: ($CDCl_3$) δ 7.02 (dd, 1H, sp^2 3-position, J(3-2) = 6.00 Hz, J(3-1) = 1.48 Hz), 6.60 (dd, 1H, sp^2 2-position, J(2-3) = 6.00 Hz, J(2-1) = 1.98 Hz), 3.71 (m, 1H, sp^3 1-position, J(1-2) = 1.98 Hz, J(1-3) = 1.48 Hz). 2.47 (s, 3H, 4-position CH_3), 2.37 (s, 3H, 7-position CH_3), 2.32 (s, 6H, overlapping 5- and 6-position CH_3), −0.04 (s, 9H, $Si(CH_3)_3$).

3.18. Synthesis of 1-trimethylsilyl-2,3,4,5,6,7-hexamethylindene (XVII)

The method of preparation was the same as for 1-trimethylsilyl-2,3-dimethylindene except that butyllithium (13.8 ml, 1.6 M in hexane, 0.022 mol) was reacted with 2,3,4,5,6,7-hexamethylindene (**VI**, 4.0 g, 0.020 mol), followed by reaction with chlorotrimethylsilane (3.2 ml, 0.025 mol). Work-up of the residue yielded 1-trimethylsilyl-2,3,4,5,6,7-hexamethylindene as a yellow oil (4.01 g, 73% yield). ^{1}H-NMR: ($CDCl_3$) δ 3.35 (s, 1H, 1-position), 2.52 (s, 3H, 4-position CH_3), 2.24 (s, 3H, 7-position CH_3), 2.21 (s, 6H, overlapping 5 and 6-position CH_3), 2.18 (s, 3H, 2-postion CH_3), 2.04 (s, 3H, 3-position CH_3), −0.10 (s, 9H, $Si(CH_3)_3$).

3.19. Synthesis of 1-trimethylsilyl-1,2,3,4,5,6,7-heptamethylindene (XVIII) [4f]

The method of preparation was the same as for 1-trimethylsilyl-2,3-dimethylindene except that butyllithium (15 ml, 1.6 M in hexane, 0.024 mol) was reacted with 1,2,3,4,5,6,7-heptamethylindene (**VII**, 5.0 g, 0.023 mol), followed by reaction with chlorotrimethylsilane (3.6 ml, 0.028 mol). Work-up of the residue yielded 1-trimethylsilyl-1,2,3,4,5,6,7-heptamethylindene as a yellow oil (4.79 g, 71% yield). ^{1}H-NMR: ($CDCl_3$) δ 2.52 (s, 3H, 4-position CH_3), 2.33 (s, 3H, 7-position CH_3), 2.25 (s, 3H, 5-position CH_3), 2.24 (s, 3H, 6-position CH_3), 2.21 (s, 3H, 2-position CH_3), 1.91 (s, 3H, 3-position CH_3), 1.565 (s, 3H, 1-position CH_3), −0.17 (s, 9H, $Si(CH_3)_3$).

3.20. Synthesis of 1-trimethylsilyl-3-allylindene (XIX)

Butyllithium (8.0 ml, 1.6 M in hexane, 0.013 mol) was added to a 100 ml solution of 1-allylindene (**VIII**, 2.0 g, 0.013 mol) in THF contained in a magnetically stirred 200 ml side-armed round bottom flask fitted with a gas-outlet valve connected to a mercury over-pressure valve. After the solution had stirred for 4 h, chlorotrimethylsilane (2.0 ml, 0.016 mol) was added to the flask via a syringe and stirring was continued overnight. The THF and excess chlorotrimethylsilane were removed under reduced pressure, replaced with 100 ml of dry hexane, and stirred for 15 min. The hexane solution was filtered using a filter cannula and the solvent was removed under reduced pressure to yield 1-trimethylsilyl-3-allylindene as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 7.55-7.15 (m, 4H, arom.), 6.38 (s, 1H, sp^2 2-position), 6.30–5.81 (complex m, 1H, sp^2, $-CH_2-C\mathbf{H}=CH_2$), 5.27 (m, 1H, sp^2, $-CH_2-CH=C\mathbf{H}_2$ *trans*), 5.17 (m, 1H, sp^2, $-CH_2-CH=C\mathbf{H}_2$ *cis*), 3.45 (s, 1H, sp^3 1-position), 3.35 (m, 2H, sp^3, $-C\mathbf{H}_2-CH=CH_2$), 0.01 (s, 9H, $Si(CH_3)_3$).

3.21. Synthesis of 1-trimethylsilyl-3-n-propylindene (XX)

The method of preparation was the same as for 1-trimethylsilyl-3-allylindene except butyllithium (8.0 ml, 1.6 M in hexane, 0.013 mol) was reacted with 1-*n*-propylindene (**IX**, 2.0 g, 0.013 mol), followed by reaction with chlorotrimethylsilane (2.0 ml, 0.016 mol). Work-up of the residue yielded 1-trimethylsilyl-3-propylindene as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 7.38 (m, 2H, arom.), 7.23 (m, 2H, arom.), 6.32 (s, 1H, sp^2 2-position, $J(2\text{-}1) = 1.8$ Hz), 3.18 (s, 1H, sp^3 1-position, $J(1\text{-}2) = 1.8$ Hz), 2.14 (t, 2H, $-C\mathbf{H}_2CH_2CH_3$, $J(1'\text{-}2') = 2.2$ Hz), 1.51 (m, 2H, $-CH_2C\mathbf{H}_2CH_3$, $J(2'\text{-}1') = 2.2$ Hz, $J(2'\text{-}3') = 3.2$ Hz), 0.96 (t, 3H, $-CH_2CH_2C\mathbf{H}_3$, $J(3'\text{-}2') = 3.2$ Hz), 0.01 (s, 9H, $Si(CH_3)_3$).

3.22. Synthesis of 1-trimethylsilyl-3-(4′-but-1′-enyl)indene (XXI)

The method of preparation was the same as for 1-trimethylsilyl-3-allylindene except that butyllithium (7.5 ml, 1.6 M in hexane, 0.012 mol) was reacted with 3-(4′-but-1′-enyl)indene (**XI**, 2.0 g, 0.012 mol), followed by reaction with chlorotrimethylsilane (1.5 ml, 0.012 mol). Work-up of the residue yielded 1-trimethylsilyl-3-(4′-but-1′-enyl)indene as a yellow oil.^{1}H-NMR ($CDCl_3$): δ 7.4–7.2 (m, 4H, arom.), 6.22 (bs, 1H, sp^2 2-position), 5.95 (m, 1H, $-CH_2CH_2C\mathbf{H}=CH_2$, $J(2'\text{-}1'trans) = 8.2$ Hz), 5.12 (d of m, 1H, $-CH_2CH_2CH=C\mathbf{H}H$ *trans*, $J(1'trans\text{-}2') = 8.2$ Hz), 4.95 (m, 1H, $-CH_2CH_2CH=C\mathbf{H}H$ *cis*), 3.42 (m, 1H, sp^3 1-position, $J(1'\text{-}4') = 1.4$ Hz), 2.8–2.4 (m of m, 4H, $-C\mathbf{H}_2C\mathbf{H}_2CH=CH_2$, overlapping signals, $J(4'\text{-}1') = 1.4$ Hz), 0.01 (s, 9H, $Si(CH_3)_3$).

3.23. Synthesis of 1-trimethylsilyl-3-n-butylindene (XXII)

The method of preparation was the same as for 1-trimethylsilyl-2,3-dimethylindene except butyllithium (7.5 ml, 1.6 M in hexane, 0.012 mol) was reacted with 1-*n*-butylindene (**X**, 2.0 g, 0.012 mol) to produce the lithium indene, followed by reaction with chlorotrimethylsilane (1.5 ml, 0.012 mol). Work-up of the residue yielded 1-trimethylsilyl-3-*n*-butyllindene as a yellow oil. ^{1}H-NMR ($CDCl_3$): δ 7.38 (m, 2H, arom.), 7.23 (m, 2H, arom.), 6.37 (s, 1H, sp^2 2-position), 3.45 (m, 1H, sp^3 1-position), 2.13 (t, 2H, $-C\mathbf{H}_2CH_2CH_2CH_3$, $J(1'\text{-}2') = 4.2$ Hz), 1.75–1.50 (m, 4H, overlapping signals $-CH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$, $J(3'\text{-}4') = 3.2$ Hz), 1.09 (t, 3H, $-CH_2CH_2CH_2C\mathbf{H}_3$, $J(4'\text{-}3') = 3.2$ Hz), 0.01 (s, 9H, $Si(CH_3)_3$).

3.24. Synthesis of 1,2-dimethylindenyltrichlorotitanium (1)

1-Trimethylsilyl-2,3-dimethylindene (**XII,** 2.0 g, 0.0092 mol) in CH_2Cl_2 (50 ml) was added dropwise via syringe to a solution of $TiCl_4$ (1.1 ml, 0.01 mol) in CH_2Cl_2 and stirred overnight producing a burgundy colored solution. The solvent, chlorotrimethyl-silane, and excess $TiCl_4$ were removed under vacuum and the crude product residue washed with 50 ml of pentane. The burgundy colored pentane solution was transferred to a Schlenk flask via filter cannula and chilled to -20°C to yield burgundy colored crystals. The remaining residue was recrystallized from pentane–CH_2Cl_2 (10:1) to yield burgundy colored crystals for a total of 2.38 g (0.008 mol, 87% yield). ^{1}H-NMR: ($CDCl_3$) δ 7.75–7.61 (m, 2H, arom.), 7.55–7.31 (m, 2H, arom.), 7.00 (s, 1H, 3-position), 2.66 (s, 3H, 1-position CH_3), 2.56 (s, 3H, 2-position CH_3). ^{13}C-NMR ($CDCl_3$): δ 13.62 (1-position CH_3), 16.82 (2-position CH_3), 116.69 (3-position C), 125.93 (4-position C), 127.84 (7-position C), 129.13 (5-position C), 129.24 (6-position C), 131.65 (9-position C), 131.75 (8-position C) 132.43 (1-position C), 140.07 (2-position C). Anal. Found (%): C, 44.17; H, 3.77. $C_{11}H_{11}Cl_3Ti$ Anal. Calc. (%): C, 44.42; H, 3.72.

3.25. Synthesis of 1,3-dimethylindenyltrichlorotitanium (2) [15]

1-Trimethylsilyl-1,3-dimethylindene (**XIII**, 2.0 g, 0.0092 mol) in CH_2Cl_2 (50 ml) was added dropwise via syringe to a solution of $TiCl_4$ (1.1 ml, 0.01 mol) in CH_2Cl_2 and stirred overnight producing a burgundy colored solution. The solvent, chlorotrimethyl-silane, and excess $TiCl_4$ were removed under vacuum and the

crude product residue washed with 50 ml of pentane. The burgundy colored pentane solution was transferred to a Schlenk flask via filter cannula and chilled to −20°C to yield burgundy colored crystals. The remaining residue was recrystallized from pentane–CH_2Cl_2 (10:1) to yield burgundy colored crystals for a total of 1.94 g (0.008 mol, 85% yield).^{1}H-NMR: ($CDCl_3$) δ 7.76 (m, 2H, arom.), 7.57 (m, 2H, arom.), 6.81 (s, 1H, 2-postion), 2.78 (s, 6H, 1 and 3-position CH_3). Anal. Found (%): C, 43.61; H, 3.92. $C_{11}H_{11}Cl_3Ti$ Anal. Calc.: C, 44.42; H, 3.72%.

3.26. Synthesis of 1,2,3-trimethylindenyltrichlorotitanium (3)

1-Trimethylsilyl-1,2,3-trimethylmethylindene (**XIV**, 2.0g, 0.0087 mol) in CH_2Cl_2 (50 ml) was added dropwise via syringe to a solution of $TiCl_4$ (1.1 ml, 0.01 mol) in CH_2Cl_2 and stirred overnight producing a green colored solution. The solvent, chlorotrimethylsilane, and excess $TiCl_4$ were removed under vacuum and the crude product residue washed with 50 ml of pentane. The purple colored pentane solution was transferred to a Schlenk flask via filter cannula and chilled to −20°C to yield purple colored crystals. The remaining residue was recrystallized from pentane to yield purple colored crystals for a total of 2.57 g (0.008 mol, 94% yield). ^{1}H-NMR: ($CDCl_3$) δ 7.83–7.65 (m, 2H, arom.), 7.60–7.42 (m, 2H, arom.), 2.72 (s, 6H, 1 and 3-position CH_3), 2.53 (s, 3H, 2-postion CH_3). ^{13}C-NMR ($CDCl_3$): δ 14.32 (1 and 3-position CH_3), 14.59 (2-position CH_3), 126.14 (4 and 7-position C), 128.72 (5 and 6-position C), 131.27 (8 and 9-position C), 132.07 (1 and 3-position C), 138.51 (2-position C). Anal. Found (%): C, 46.13; H, 4.01. $C_{12}H_{13}Cl_3Ti$ Anal. Calc. (%): C, 46.27; H, 4.21.

3.27. Synthesis of 1,3,4,7-tetramethylindenyltrichlorotitanium (4)

1-Trimethylsilyl-1,3,4,7-tetramethylindene (**XV**, 2.0 g, 0.0082 mol) in CH_2Cl_2 (50 ml) was added dropwise via syringe to a solution of $TiCl_4$ (1.1 ml, 0.01 mol) in CH_2Cl_2 and stirred overnight producing a green colored solution. The solvent, chlorotrimethylsilane, and excess $TiCl_4$ were removed under vacuum and the crude product residue washed with 50 ml of pentane. The purple colored pentane solution was transferred to a Schlenk flask via filter cannula and chilled to −20°C to yield purple colored crystals. The remaining residue was recrystallized from pentane to yield purple colored crystals for a total of 2.22 g (0.0068 mol, 83% yield). ^{1}H-NMR: ($CDCl_3$) δ 7.05 (s, 2H, 5 and 6-positions), 6.65 (s, 1H, 2-position), 2.91 (s, 6H, 1 and 3-position CH_3), 2.70 (s, 6H, 4 and 7-position CH_3). Anal. Found (%): C, 48.30; H, 4.86. $C_{13}H_{15}Cl_3Ti$ Anal. Calc. (%): C, 47.96; H, 4.64.

3.28. Synthesis of 4,5,6,7-tetramethylindenyltrichlorotitanium (5)

1-Trimethylsilyl-4,5,6,7-tetramethylindene (**XVI**, 2.0 g, 0.0082 mol) in CH_2Cl_2 (50 ml) was added dropwise via syringe to a solution of $TiCl_4$ (1.1 ml, 0.01 mol) in CH_2Cl_2 and stirred overnight producing a green colored solution. The solvent, chlorotrimethylsilane, and excess $TiCl_4$ were removed under vacuum and the crude product residue washed with 50 ml of pentane. The purple colored pentane solution was transferred to a Schlenk flask via filter cannula and chilled to −20°C to yield purple colored crystals. The remaining residue was recrystallized from pentane to yield purple colored crystals for a total of 2.62 g (0.008 mol, 98% yield). ^{1}H-NMR: ($CDCl_3$) δ 7.09 (d, 2H, 1 and 3-positions), 7.01 (t, 1H, 2-position), 2.53 (s, 6H, 4 and 7-position CH_3), 2.38 (s, 6H, 5 and 6-position CH_3). Anal. Found (%): C, 47.94; H, 4.43. $C_{13}H_{15}Cl_3Ti$ Anal Calc. (%): C, 47.97; H, 4.65.

3.29. Synthesis of 1,2,4,5,6,7-hexamethyltrichlorotitanium (6)

1-Trimethylsilyl-2,3,4,5,6,7-hexamethylindene (**XVII**, 1.0 g, 0.0037 mol) in CH_2Cl_2 (50 ml) was added dropwise via syringe to a solution of $TiCl_4$ (1.1 ml, 0.01 mol) in CH_2Cl_2 and stirred overnight producing a green colored solution. The solvent, chlorotrimethylsilane, and excess $TiCl_4$ were removed under vacuum and the crude product residue washed with 50 ml of pentane. The purple colored pentane solution was transferred to a Schlenk flask via filter cannula and chilled to −20°C to yield purple colored crystals. The remaining residue was recrystallized from pentane to yield purple colored crystals for a total of 0.983 g (0.0028 mol, 75% yield). ^{1}H-NMR: ($CDCl_3$) δ 6.90 (s, 1H, 3-position), 2.86 (s, 3H, 1-position CH_3), 2.68 (s, 3H, 2-position CH_3), 2.53 (s, 3H, 7-position CH_3), 2.47 (s, 3H, 4-position CH_3), 2.38 (s, 3H, 6-position CH_3), 2.35 (s, 3H, 5-position CH_3). Anal. Found (%): C, 51.31; H, 5.73. $C_{15}H_{19}Cl_3Ti$ Anal. Calc. (%): C, 50.96; H, 5.42.

3.30. Synthesis of 1,2,3,4,5,6,7-heptamethylindenyltrichlorotitanium (7) [4f]

1-Trimethylsilyl-1,2,3,4,5,6,7-heptamethylindene (**XVIII**, 2.0 g, 0.0070 mol) in CH_2Cl_2 (50 ml) was added dropwise via syringe to a solution of $TiCl_4$ (1.1 ml, 0.01 mol) in CH_2Cl_2 and stirred overnight producing a green colored solution. The solvent, chlorotrimethylsilane, and excess $TiCl_4$ were removed under vacuum and the crude product residue washed with 50 ml of pentane. The green colored pentane solution was transferred to a Schlenk flask via filter cannula and chilled to −20°C to

yield green colored crystals. The remaining residue was recrystallized from pentane to yield green colored crystals for a total of 2.08 g (0.0057 mol, 81% yield). ^{1}H-NMR: ($CDCl_3$) δ 2.53 (s, 6H, 1 and 3-position CH_3), 2.49 (s, 3H, 2-position CH_3), 2.37 (s, 6H, 4 and 7-position CH_3), 2.36 (s, 6H, 5 and 6-position CH_3). Anal. Found (%): C, 52.75; H, 5.79. $C_{16}H_{21}Cl_3Ti$ Anal. Calc. (%): C, 52.28; H, 5.76.

3.31. Synthesis of 1-allylindenyltrichlorotitanium (9)

$TiCl_4$ (3.2 ml, 0.029 mol) was added via syringe to 100 ml of CH_2Cl_2 in a 250-ml side-armed Schlenk flask that was fitted with a gas outlet valve connected to a mercury overpressure bubbler. 1-Trimethylsilyl-3-allylindene (**XIX**, 6.4 g, 0.028 mol) was then added and the dark burgundy solution allowed to react overnight at room temperature. After the solvent was removed under vacuum, the burgundy residue was washed with 50 ml of pentane and dried under vacuum. Recrystallization of the residue from pentane afforded 7.63 g (88% yield) of dark red crystals. ^{1}H-NMR ($CDCl_3$): δ 7.78 (m, 2H, arom.), 7.51 (m, 2H, arom.), 7.15 (d, 1H, 3-position, J(3-2) = 3.4 Hz), 6.97 (d, 1H, 2-position, J(2-3) = 3.4 Hz), 6.04 (m, 1H, sp^2, $-CH_2C\mathbf{H}=CH_2$, J(2′-3′) = 5.8 Hz, J(2′-1′*trans*) = 6.4 Hz) 5.27 (dm, 1H, sp^2, $-CH_2CH=C\mathbf{H}_2$ *cis*, J(1′-1′*gem*) = 1.8 Hz), 5.10 (dm, 1H, sp^2, $-CH_2CH=C\mathbf{H}_2$ *trans*, J(1′-2′ *trans*) = 6.4 Hz, J(1′-1′*gem*) = 1.8 Hz), 3.93 (dm, 2H, sp^3, $-C\mathbf{H}_2CH=CH_2$, J(3′-2′) = 5.8 Hz). Anal. Found (%): C, 46.83; H, 3.68. $C_{12}H_{11}Cl_3Ti$ Anal. Calc. (%): C, 46.57; H, 3.58.

3.32. Synthesis of 1-n-propylindenyltrichlorotitanium (10)

The method of preparation was the same as for 1-allylindenyltrichlorotitanium except that $TiCl_4$ (3.2 ml, 0.029 mol) was reacted 1-trimethylsilyl-3-propylindene (**XX**, 5.75 g, 0.025 mol), which upon work-up afforded 7.16 g (92%) of dark red crystals. ^{1}H-NMR ($CDCl_3$): δ 7.80 (m, 2H, arom.), 7.56 (m, 2H, arom.), 7.15 (d, 1H, 3-position, J(3-2) = 3.0 Hz), 6.98 (d, 1H, 2-position, J(2-3) = 3.0 Hz), 3.15 (t, 2H, 1′-position, J(1′-2′) = 8.2 Hz), 1.79 (m, 2H, 2′-position, J(2′-3′) = 7.3 Hz, J(2′-1′) = 8.2 Hz), 1.04 (t, 3H, 3′-position, J(3′-2′) = 7.3 Hz). Anal. Found (%): C, 46.69; H, 4.35. $C_{12}H_{13}Cl_3Ti$ Anal. Calc. (%): C, 46.27; H, 4.21.

3.33. Synthesis of 1-(4′-but-1′-enyl)indenyltrichlorotitanium (11)

The method of preparation was the same as for 1-allylindenyltrichlorotitanium except that $TiCl_4$ (3.2 ml, 0.029 mol) was reacted with 1-trimethylsilyl-3-(4′-but-1′-enyl)indene (**XXI**, 6.8 g, 0.028 mol), which upon work-up afforded 8.79 g (97%) of dark red crystals. ^{1}H-NMR ($CDCl_3$): δ 7.80 (m, 2H, arom.), 7.52 (m, 2H, arom.), 7.13 (d, 1H, 3-position, J(3-2) = 3.4 Hz), 6.97 (d, 1H, 2-position, J(2-3) = 3.4 Hz), 5.85 (m, 1H, 2′-position, J(2′-3′) = 8.8 Hz, J(2′-1′*trans*) = 3.6 Hz), 5.12 (dm, 1H, 1′-position *trans*, J(1′-2′*trans*) = 3.6 Hz, J(1′-1′*gem*) = 1.3 Hz), 4.96 (m, 1H, 1′-position *cis*, J(1′-1′*gem*) = 1.3 Hz), 3.27 (t, 2H, 4′-position, J(4′-3′) = 8.9 Hz), 2.51 (m, 2H, 3′-position, J(3′-4′) = 8.9 Hz, J(3′-2′) = 8.8 Hz). Anal. Found (%): C, 48.46; H, 3.64. $C_{13}H_{13}Cl_3Ti$ Anal. Calc. (%): C, 48.27; H, 4.05.

3.34. Synthesis of 1-n-butylindenyltrichlorotitanium (12)

The method of preparation was the same as for 1-allylindenyltrichlorotitanium except that $TiCl_4$ (3.2 ml, 0.029 mol) was reacted with 1-trimethylsily-3-butyllindene (**XXII**, 6.6 g, 0.027 mol). Recrystallization of the residue from a minimum volume of CH_2Cl_2 afforded 8.09 g (92%) of dark red crystals. ^{1}H-NMR ($CDCl_3$): δ 7.80 (m, 2H, arom.), 7.53 (m, 2H, arom.), 7.14 (d, 1H, 3-position, J(3-2) = 3.3 Hz), 6.97 (d, 1H, 2-position, J(2-3) = 3.3 Hz), 3.17 (t, 2H, 1′-position, J(1′-2′) = 7.5 Hz), 1.72 (m, 2H, 2′-position, J(2′-1′) = 7.5 Hz, J(2′-3′) = 7.4 Hz), 1.44 (m, 2H, 3′-position, J(3′-4′) = 11.9 Hz, J(3′-2′) = 7.4 Hz), 0.98 (t, 3H, 4′-position, J(4′-3′) = 11.9 Hz). Anal. Found (%): C, 48.45; H, 4.76. $C_{13}H_{15}Cl_3Ti$ Anal. Calc. (%): C, 47.99; H, 4.65.

3.35. Synthesis of indenyltrimethyltitanium (13)

Indenyltrichlorotitanium (5.0g, 0.0185 mol) was dissolved in 150 ml of diethyl ether and contained in a 250 ml side-armed round bottomed flask fitted with a mercury overpressure bubbler and cooled to −78°C. Methyllithium (39.6 ml, 1.4 M in ether, 0.0555 mol) was added via syringe and the yellow colored solution stirred for 2 h. After warming to 0°C, the ether was removed by vacuum and replaced with 50 ml of cold pentane. The slurry was stirred for 15 min while maintaining the temperature at 0°C. The yellow colored solution was filtered using a filter cannula and stored at −20°C overnight. The supernatant mother liquor was removed and the yellow colored crystals were dried by blowing argon over them for 15 min while maintaining a cold temperature. The crystals were very temperature sensitive, turning to a white powder at room temperature after an hour. ^{1}H-NMR: (C_6D_6) δ 7.23 (m, 2H, 4 and 7-positions), 6.95 (m, 2H, 5 and 6 positions), 5.74 (d, 2H, 1 and 3-positions, J(1,3-2) = 3.2 Hz), 5.38 (t, 1H, 2-position, J(2-1,3) = 3.2 Hz), −0.50 (s, 9H, CH_3). Anal. Found (%): C, 68.41; H, 5.89. $C_{12}H_{16}Ti$ Anal. Calc. (%): C, 69.25; H, 7.75.

3.36. Synthesis of indenyldichloromethyltitanium (**14**)

Indenyltrichlorotitanium (5.0 g, 0.0185 mol) was dissolved in 150 ml of diethyl ether contained in a 250 ml side-armed round bottomed flask fitted with a mercury overpressure bubbler and cooled to −78°C. Methyllithium (13.2 ml, 1.4 M in ether, 0.0185 mol) was added via syringe and the yellow colored solution stirred for 2 h. After warming to 0°C, the ether was removed by vacuum and replaced with 50 ml of cold pentane. The slurry was stirred for 15 min while maintaining the temperature at 0°C. The cold orange solution was filtered using a filter cannula and stored at −20°C overnight. The supernatant mother liquor was removed and the orange colored crystals were dried under vacuum. The total yield from the mother liquor was 4.38 g (95%). ^{1}H-NMR: (C_6D_6) δ 7.38 (m, 2H, 4 and 7 positions), 7.08 (m, 2H, 5 and 6 positions), 6.55 (d, 2H, 1 and 3-positions, $J(1,3\text{-}2) = 7.1$ Hz), 6.30 (t, 1H, 2-position, $J(2\text{-}1,3) = 7.1$ Hz), 1.75 (s, 3H, CH_3). Anal. Found (%): C, 47.62; H, 4.25. $C_{10}H_{10}Cl_2Ti$ Anal. Calc. (%): C, 48.24; H, 4.05.

3.37. Synthesis of (η^5-indenyl)(η^7-cycloheptatrienyl)titanium (**15**) [17]

Cycloheptatriene (1.0 ml, 0.0096 mol) was added to Mg turnings (3.65 g, 0.15 mol) in 100 ml of THF contained in a 300 ml side-armed flask equipped with a magnetic stirrer and a gas outlet valve connected to a Hg over pressure bubbler, and the mixture stirred for 15 min. $IndTiCl_3$ (2.0 g, 0.0074 mol) in 100 ml of THF was added to the flask and stirred for approximately 30 min during which time the color of the reaction mixture turned from orange to black. The THF was removed under reduced pressure, replaced with 200 ml of toluene, and stirred vigorously for 15 min. The reaction mixture was filtered over a 5 cm silica plug which had been previously washed with toluene, to yield a bright green solution. The green solution was concentrated and chilled to −20°C after which green crystals crystals of $IndTi(C_7H_7)$ formed (total yield = 0.46 g, 0.0018 mol, 24%). The product can also be purified by vacuum sublimation (70°C, 0.002 mmHg). ^{1}H-NMR: (C_6D_6) δ 7.11 (m, 2H, arom.), 6.71 (m, 2H, arom.), 5.31 (d, 2H, indenyl 1 and 3-positions), 5.26 (s, 7H, cycloheptatrienyl), 5.09 (t, 1H, indenyl 2-position). Anal. Found (%): C, 75.84; H, 5.72. $C_{10}H_{10}Cl_2Ti$ Anal. Calc. (%): C, 75.61; H, 5.55.

3.38. Styrene polymerizations

Polymerizations of styrene using the various catalyst precursors were carried out by injecting 42 ml of toluene, followed by an injection of 5.0 ml of styrene (previously dried over CaH_2 for 12 h and distilled from CaH_2), followed by an injection of 3.2 ml of 3.1 M MAO, into 250 ml crown capped pressure bottles sealed under inert atmosphere and brought to constant 50°C. At this time the solutions were stirred for 10 min to scavenge impurities. Polymerizations were initiated by injection of 0.5 ml of 5 mM titanium precursor solution. Polymerization reactions were run for 30 min and quenched by the addition of 100 ml of 10% HCL/methanol. The resulting polymers were filtered, dried, and weighed (for calculation of activity). The bulk polymers were extracted using a Soxhlet extractor for 12 h in 2-butanone, dried, and weighed (for calculation of the percentage syndiotactic polystyrene) [3a, 28, 29, 30].

3.39. Ethylene polymerizations

Polymerizations of ethylene using the various catalyst precursors were carried out by injecting 46.8 ml of toluene followed by injection of 3.2 ml of 3.1 M MAO into 250 ml crown capped pressure bottles sealed under inert atmosphere and brought to constant polymerization temperature. At this time the solutions were stirred for 10 min to scavenge impurities. The pressure bottle was degassed via vacuum followed by pressurization with ethylene (15 psig) and the system allowed to equilibrate for 20 min. The degassing/pressurization procedure was repeated twice more. Polymerizations were initiated by the injection of 0.5 ml of 5 mM titanium precursor solution. Polymerization reactions were run for 2 h and quenched by the addition of 100 ml of 10% HCL/methanol. The resulting polymers were filtered, dried, and weighed (for calculation of activity).

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[28] It is well established that 2-butanone insoluble polystryrene is either syndiotactic [1] or isotactic [29]. The tacticity can be established either by ^{13}C-NMR [3a] or by the melting tempera-

ture (T_m) of the polymer; T_m(*s*-PS)/270°C, T_m(*i*-PS)/240°C [30]. The T_m for the various 2-butanone insoluble polymers obtained in this study are reported in Table 1 and establish that these polymers are indeed *s*-PS.

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