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Alkyl-substituted indenyl titanium precursors for syndiospecific Ziegler–Natta polymerization of styrene

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Abstract

A variety of 1- and 3-substituted alkylindenes (R = H, Me, Et, *tert*-butyl, Me_3Si) as well as 2-methylindene and 3-(methylthio)indene 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, $(R-Ind)TiCl_3$, were synthesized in excellent yield 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. Activities increased in the order: Cp < H_4Ind < Ind < 1-(Me)Ind < 2-(Me)Ind. A steep drop in activity was observed when R = Et, *tert*-butyl, and Me_3Si, corresponding to an increase in the steric bulk of the substituent in the catalyst precursor. 1-(MeS)Ind$TiCl_3$ was found to be ineffective as a styrene polymerization catalyst. Syndiospecificities of the titanium complexes were generally very good (65–98%).

Keywords: Titanium; Lithium; Indenyl complexes; Styrene; Polymerization

1. Introduction

In recent years (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 [1]. Several groups have observed that replacement of a cyclopentadienyl ligand by an indenyl ligand in various organometallic complexes resulted in significant enhancement of the rate of ligand substitution [2]. We recently synthesized (η^5-indenyl)trichlorotitanium, Ind$TiCl_3$, and demonstrated that replacing a cyclopentadienyl ligand by an indenyl ligand in this series doubled the catalytic activity, increased the syndiospecificity, and stabilized the resulting catalyst at elevated temperatures in styrene polymerizations compared with $CpTiCl_3$ [3]. In order to investigate more fully this phenomenon, we have synthesized a variety of alkyl-substituted indenyltrichlorotitanium complexes, and have compared their relative catalytic activities toward styrene when activated with methylaluminoxane (MAO).

2. Results

2.1. Synthesis of catalyst precursors

1- and 3-substituted alkylindenes [4] (Scheme 1), 1-(trimethylsilyl)indene [5] (Scheme 1), 2-methylindene [6] (Scheme 2), and 1-(methylthio)indene [7] (Scheme 1) were prepared in 75–98% yields using modifications of literature methods. In the case of methyl-, ethyl-, and *tert*-butyllindenes, the specific 1- or 3-isomers isolated were found to be solvent mediated. The substituted indenes were converted into trimethylsilyl derivatives via reactions of intermediate organolithium analogs with chlorotrimethylsilane. The corresponding titanium complexes were synthesized in excellent yields via reactions of the trimethylsilylindene derivatives with $TiCl_4$, using procedures described for analogous cyclopentadienyltitanium complexes [8] (Schemes 1 and 2). 4,5,6,7-Tetrahydroindenyltrichlorotitanium (H_4-Ind$TiCl_3$) was syn-

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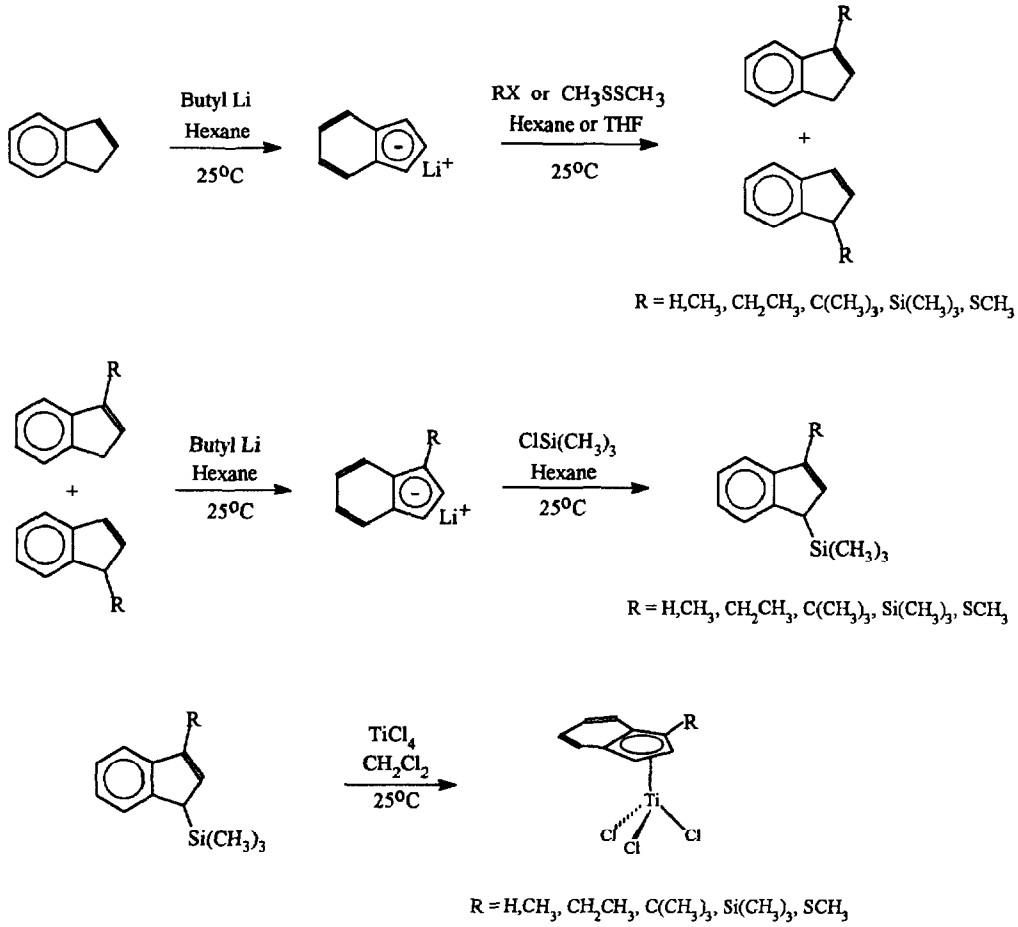
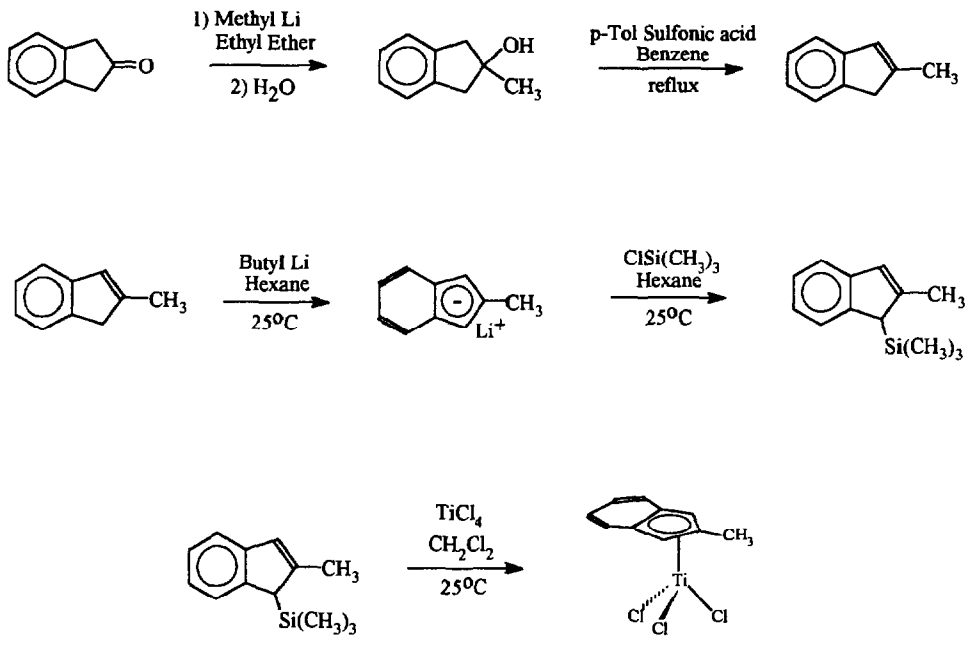
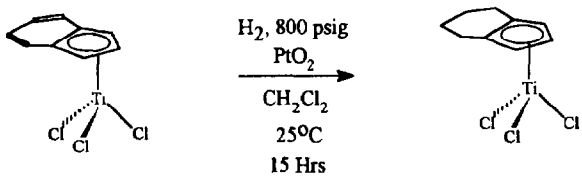


Scheme 1.



Scheme 2.



Scheme 3.

thesized in quantitative yield using an approach similar to that described by Samuel [9] (Scheme 3). Synthetic details and ^{1}H NMR spectral data for these compounds are given in the Experimental section.

2.2. Polymerization results

Comparative polymerizations of styrene using the various catalyst precursors were carried out by injecting 42 ml of toluene, followed by injection of 5.0 ml of styrene (previously dried over CaH_2 for 12 h and distilled from CaH_2), 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 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 percentage syndiotactic polystyrene) [10]. These results are summarized in Table 1.

Activation of a catalyst precursor does not always occur immediately. In order to compensate for any possible differences in activation times for the various precursors, and obtain a better comparison of the relative activities of the catalyst precursors, we also 'aged' or 'preactivated' the catalyst before exposure to monomer solution. Preactivation and polymerization were carried out in separate bottles.

Preactivations were conducted by injecting 31.9 ml of toluene, followed by 8.1 ml of 3.1 M MAO into bottle 1 (previously sealed under inert atmosphere) and the solution stirred for 10 min to scavenge impurities. 10 ml of the titanium precursor solution (1.25 mM) was injected into bottle 1 and stirred for 10 min to achieve activation.

The polymerizations were carried out by injecting 33.4 ml of toluene, followed by injection of 5.0 ml of styrene (purified as described above), followed by injection of 1.5 ml of 3.1 M MAO into bottle 2 (previously sealed under an inert atmosphere), and the solution stirred for 10 min to scavenge impurities. Polymerizations were initiated by transfer of 10 ml of activated titanium catalyst solution (bottle 1) to bottle 2 via syringe. The polymerization was quenched after 10 min by the addition of 100 ml of 10% HCl–methanol. These polymerization results are summarized in Table 2.

Table 1
Styrene polymerizations catalyzed by $LTiCl_3$ activated with MAO [a]

L [b]	Total yield (g)	A [c] ($\times 10^{-7}$)	s-PS [d] (%)	T_m [e] (°C)	M_w [f] ($\times 10^{-3}$)
Cp	0.749	1.4	67.4	251.5, 259.7	435
H_4Ind	0.992	2.7	89.1	261.5, 270.9	620
Ind	2.039	3.7	98.2	264.6, 270.8	720
1-(Me)Ind	2.791	5.1	89.5	262.5, 271.9	650
2-(Me)Ind [g]	4.426	16.6	90.2	262.5, 272.2	660
1-(Et)Ind	1.436	2.6	82.0	262.5, 272.3	430
1-(Me_3C)Ind	0.108	0.196	64.8	261.7, 271.2	95
1-(Me_3Si)Ind	0.402	0.73	86.4	260.7, 268.0	125
1-(MeS)Ind	0.100	0.183	80.5	260.3, 268.1	14

[a] Polymerization conditions: [Ti] = 50 μM; [Al]/[Ti] = 4000; reaction time = 0.5 h; T_p = 50 °C; [styrene] = 0.87 M.
[b] Cp = η^5-cyclopentadienyl; H_4Ind = η^5-4,5,6,7-tetrahydroindenyl; Ind = η^5-indenyl; Me = methyl; Et = ethyl; Me_3C = *tert*-butyl; Me_3Si = trimethylsilyl; MeS = methylthio.
[c] A (activity) = (g bulk polymer)/(mol Ti)(mol monomer)(h).
[d] Percentage s-PS = [(g of 2-butanone insoluble polymer)/(g of bulk polymer)] × 100.
[e] T_m, melting temperature of s-PS.
[f] M_w, calculated by first using solution viscometry to determine the intrinsic viscometries of the polymers, then using the Mark–Houwink equation.
[g] Reaction time = 15 min due to inability to stir the reaction solution.

Table 2
Styrene polymerizations catalyzed by $LTiCl_3$ preactivated with MAO [a,b]

L [c]	Total yield (g)	A [d] ($\times 10^{-7}$)	s-PS [e] (%)
Cp	0.989	5.46	89.2
H_4Ind	1.594	8.80	94.5
Ind	2.735	15.1	98.1
1-(Me)Ind	3.115	17.2	94.2
2-(Me)Ind	4.502	24.9	94.7
1-(Et)Ind	1.648	9.10	92.3
1-(Me_3C)Ind	0.176	0.97	89.7
1-(Me_3Si)Ind	0.203	1.12	90.3
1-(MeS)Ind	0.00	–	–

[a] Preactivation conditions: [Ti] = 2.5 mM; [Al]/[Ti] = 2000; reaction time = 0.16166 h; T_a = 25 °C; styrene solution scavenged with 0.1 M = [MAO].
[b] Polymerization conditions: [Ti] = 50 μM; [Al]/[Ti] = 2000; reaction time = 0.166h; T_p = 50°C; [styrene] = 0.87 M.
[c] Cp = η^5-cyclopentadienyl; H_4Ind = 4,5,6,7-tetrahydroindenyl; Ind = η^5-indenyl; Me = methyl; Et = ethyl; Me_3C = *tert*-butyl; Me_3Si = trimethylsilyl; MeS = methylthio.
[d] A (activity) = (g of bulk polymer)/(mol Ti)(mol monomer)(h).
[e] Percentage s-PS = [(g of 2-butanone insoluble polymer)/(g of bulk polymer)] × 100.

3. Discussion

The present results demonstrate the importance of both electronic and steric effects in styrene polymerizations promoted by alkyl-substituted indenyltrichlorotitanium compounds when activated by MAO. The increase in activities of Cp < H_4Ind < Ind < 1-(Me)Ind complexes is consistent with the concept that electron-releasing alkyl groups enhance the activity at the electrophilic metal center, and in general increase the syndiospecificity as well. Remarkably, 2-(Me)IndTiCl_3 is significantly more active than is 1-(Me)IndTiCl_3. Similar results are observed for other structurally related complexes, and reasons for these differences are under current investigation.

Although ethyl and *tert*-butyl substituents also have electron-releasing properties, the results in both Tables 1 and 2 indicate a steep drop in activity corresponding to an increase in the steric bulk of the substituent on the catalyst precursor. The bulky trimethylsilyl substituent also has a correspondingly low activity. An increase in the steric bulk of a substituent could interfere with monomer coordination and/or migratory insertion processes. In the absence of a bulky substituent, the η^5-ligand can rotate more or less freely to a low energy transition state geometry. A bulky substituent could present a barrier for this process.

The substituents in the complexes 1-(Et)IndTiCl_3 and 1-(MeS)IndTiCl_3 have similar steric bulk, but the former exhibits much greater activity than does the latter. The presence of lone pairs of electrons on the sulfur atom presumably have a deleterious effect on the catalytic activity in these systems. A similar result was observed previously when $(C_5H_4NMe_2)_2TiCl_2$ was found to exhibit much lower catalyst efficiency for ethylene polymerization compared with Cp_2TiCl_2 [12]. In both cases, Lewis acid–base interaction between the lone pairs of electrons on the substituent with MAO could be responsible for these results.

4. Experimental section

All operations were carried out under an 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 from 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. Melting points of polymers were determined using a Perkin–Elmer Model DSC-4 differential scanning calorimeter.

4.1. Synthesis of indenyllithium

n-Butyllithium (102 ml, 1.6 M, 0.16 mol) was added via syringe to a 500 ml side-armed round bottom flask fitted with an overpressure bubbler containing 250 ml of hexane. After the solution was slightly chilled using an ice bath, 19 ml (0.16 mol) of freshly distilled indene was added and the mixture was allowed to stir overnight at room temperature. The supernatant liquid was decanted and the white precipitate was washed three times with 150 ml portions of fresh hexane. The white precipitate (19.5 g, 99%) was dried under vacuum and stored in a glove box for future use.

4.2. Synthesis of 1-methylindene

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. Iodomethane (5.1 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 9.1 g (86%) of a yellow oil. The product was distilled at 45–46 °C/0.001 mm Hg and a colorless oil was obtained which turned yellow on standing at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.4–7.0 (m, 4H, arom.), 6.77 (dd, 1H, sp^2 3-position, J(3–2) = 5.6 Hz, J(3–1) = 1.6 Hz), 6.46 (dd, 1H, sp^2 2-position, J(2–3) = 5.6 Hz, J(2–1) = 1.6 Hz), 3.50 (q of t, 1H, sp^3 1-position, J(1–(CH_3)) = 12 Hz, J(1,2,&3) = 0.16 Hz), 1.30 (d, 3H, J((CH_3)–1) = 12 Hz).

4.3. Synthesis of 3-methylindene

THF (250 ml) was added to 10.0 g (0.082 mol) of indenyllithium in a 500 ml side-armed flask fitted with an overpressure bubbler and previously chilled to 0 °C. Iodomethane (10.3 ml, 0.165 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 9.7 g (91%) of a yellow oil. This residue was distilled at 45–46 °C/0.001 mm Hg giving a colorless oil which turned yellow on standing at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.4–7.1 (m, 4H, arom.), 6.11 (m, 1H, sp^2 2-position, J(2–1) = 1.6 Hz, J(2–(CH_3)) = 1.6 Hz), 3.22 (m, 2H, sp^3 1-position, J(1–2) = 1.6 Hz, J(1–(CH_3)) = 1.6 Hz), 2.10 (dd, 3H, CH_3, J((CH_3)–1) = 1.6 Hz, J((CH_3)–2) = 1.6 Hz).

4.4. Synthesis of 2-methylindene

Methyllithium (5.4 ml, 1.4 M) was added dropwise via a syringe to a solution of 2-indanone [6a] (10.0 g, 0.076 mol) in 250 ml of diethyl ether (previously chilled to 0 °C) and contained in a 500 ml side-armed flask fitted with a reflux condenser and overpressure bubbler. After the addition was complete, the reaction mixture was heated at reflux for 4 h. The solution was cooled to 0 °C and 200 ml of water was added dropwise. The water layer was washed twice with 50 ml portions of ether and the ether layers were combined with the original ether layer. The ether was removed at reduced pressure and replaced with 250 ml of benzene. *p*-Toluenesulfonic acid (5.0 mg) was added to the benzene solution which was then refluxed overnight using a conventional Dean–Stark apparatus to remove the water produced. The remaining benzene solution was washed with 100 ml of saturated Na_2CO_3 solution and dried over magnesium sulfate. The benzene was removed at reduced pressure and the residue (7.62 g, 77%) was distilled at 45–46 °C/0.001 mm Hg to yield a colorless oil which darkened on standing at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.45–7.07 (m, 4H, arom.) 6.52 (br s, sp^2 3-position), 3.25 (br s, 2H, sp^3 1-position), 2.15 (s, 3H, CH_3).

4.5. Synthesis of 1-ethylindene

The method of preparation was the same as for 1-methylindene except that 6.1 ml (0.082 mol) of bromoethane was used instead of iodomethane. The crude yield of 1-ethylindene was 9.23 g (78%), obtained as a yellow oil. A colorless oil was obtained via distillation at 55–56 °C/0.001 mm Hg which darkened on standing at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.35–7.02 (m, 4H, arom.), 6.70 (dd, 1H, sp^2 2-position, $J(3–2)$ = 5.6 Hz, $J(3–1)$ = 1.8 Hz), 6.42 (dd, 1H, sp^2 2-position, $J(2–3)$ = 5.6 Hz, $J(2–1)$ = 1.8 Hz), 3.29 (tt, 1H, sp^3 1-position, $J(1–(CH_2))$ = 8.0 Hz, $J(1–2\&3)$ = 1.8 Hz), 2.11–1.10 (m, 2H, CH_2), 0.93 (t, 3H, CH_3, $J(CH_3–CH_2)$ = 8.0 Hz).

4.6. Synthesis of 3-ethylindene

The preparation of 3-ethylindene was the same as that for 3-methylindene except that 12.3 ml (0.165 mol) of bromoethane was used instead of iodomethane. The yellow oil obtained (10.4 g, 89%) was distilled at 55–56 °C/0.001 mm Hg to give a colorless oil which darkened on standing at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.40–7.05 (m, 4H, arom.), 6.15 (m, 1H, sp^2 2-position), 3.27 (m, 2H, sp^3 1-position) 2.54 (q, 2H, CH_2, $J(CH_2–CH_3)$ = 8 Hz), 1.25 (t, 3H, CH_3, $J(CH_3–CH_2)$ = 8 Hz).

4.7. Synthesis of a mixture of 1-tert-butylindene and 3-tert-butylindene

The preparation of *tert*-butylindene was the same as that for 1-methylindene except that 8.9 ml (0.082 mol) of 2-chloro-2-methylpropane was used instead of iodomethane. A yellow oil was obtained (6.35 g, 45%) which was distilled at 65–68 °C/0.001 mm Hg to give a pale yellow oil. ^{1}H NMR analysis of the original crude product showed it to be almost exclusively 1-*tert*-butylindene, whereas the distilled product was a mixture of isomers, 1-*tert*-butylindene/3-*tert*-butylindene 70:30. ^{1}H NMR of 1-*tert*-butylindene ($CDCl_3$): δ 7.61–7.12 (m, 4H, arom.), 6.79 (dd, 1H, sp^2 3-position, $J(3–2)$ = 5.8 Hz, $J(3–1)$ = 1.8 Hz), 6.52 (dd, 1H, sp^2 2-position. $J(2–3)$ = 5.8 Hz, $J(2–1)$ = 1.8 Hz), 3.51 (t, 1H, sp^3 1-position, $J(1–2\&3)$ = 1.8 Hz), 1.02 (s, 9H, $3CH_3$). ^{1}H NMR of 3-*tert*-butylindene ($CDCl_3$): δ 7.69–7.35 (m, 4H, arom.), 6.19 (t, sp^2 2-position, $J(2–1)$ = 1.5 Hz), 3.26 (d, 2H, sp^3 1-position, $J(1–2)$ = 1.5 Hz), 1.37 (s, 9H, $3CH_3$).

4.8. Synthesis of 3-tert-butylindene

The preparation of *tert*-butylindene was the same as that for 3-methylindene except that 8.9 ml (0.082 mol) of 2-chloro-2-methylpropane was used instead of iodomethane. The product was isolated as a yellow oil (7.2 g, 51%). ^{1}H NMR ($CDCl_3$): δ 7.69–7.35 (m, 4H, arom.), 6.19 (t, sp^2 2-position, $J(2–1)$ = 1.5 Hz), 3.26 (d, 2H, sp^3 1-position, $J(1–2)$ = 1.5 Hz), 1.37 (s, 9H, $3CH_3$).

4.9. Synthesis of 3-(methylthio)indene

The preparation of 3-(methylthio)indene was the same as that for 1-methylindene except that 7.4 ml (0.082 mol) of dimethyldisulfide was used instead of iodomethane. The crude product was obtained as a yellow-brown oil (10.04 g, 76%) which was subsequently distilled at reduced pressure (68–70 °C/0.001 mm Hg) to give a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.50–7.10 (m, 4H, arom.), 6.07 (t, 1H, sp^2 2-position, $J(2–1)$ = 2.4 Hz), 3.30 (d, 2H, sp^3 1-position, $J(1–2)$ = 2.4 Hz), 2.36 (s, 3H, $S–CH_3$).

4.10. Synthesis of 1-(trimethylsilyl)indene

The method of preparation was the same as that for 1-methylindene except that 10.4 ml (0.082 mol) of chlorotrimethylsilane was used instead of iodomethane. A pale yellow oil (12.94 g, 85%) was obtained. Upon distillation at 78–80 °C/0.3 mm Hg, a colorless oil was obtained which turned yellow upon standing at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.5–7.15 (m, 4H,

arom.), 6.95 (d, 1H, sp^2 3-position, $J(3-2) = 3$ Hz), 6.65 (d, 1H, sp^2 2-position, $J(2-3) = 3$ Hz), 3.55 (s, 1H, sp^3 1-position), 0.01 (s, 9H, $Si(CH_3)_3$).

4.11. Synthesis of 1-trimethylsilyl-3-methylindene

1-Methylindene (5.0 g, 0.038 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, 24.1 ml of 1.6 M *n*-butyllithium (0.038 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 over a Celite plug and the solvent removed under vacuum, leaving 6.52 g (85%) of a yellow oil. The crude product was further purified via distillation at 75–76 °C/0.001 mm Hg to yield a colorless oil which darkened on standing at room temperature. ^{1}H NMR ($CDCl_3$): δ 7.55–7.11 (m, 4H, arom.), 6.35 (m, 1H, sp^2 2-position), 3.40 (m, 1H, sp^3 1-position), 2.28 (dd, 3H, CH_3 3-position, $J(CH_3-2) = 1.6$ Hz, $J(CH_3-1) = 2.1$ Hz), 0.00 (s, 9H, $Si(CH_3)_3$).

4.12. Synthesis of 1-trimethylsilyl-2-methylindene

The method of preparation was the same as that for 1-trimethylsilyl-3-methylindene except that 24.1 ml (0.038 mol) of 1.6 M *n*-butyllithium was added to 5.0 g (0.038 mol) of 2-methylindene. The crude product was obtained as a yellow oil (5.46 g, 71%) which was further purified by distillation at 90–93 °C/0.001 mm Hg giving a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.9–7.2 (m, 4H, arom.), 6.40 (d, 1H, sp^2 3-position, $J(3-1) = 2.1$ Hz), 3.43 (d, 1H, sp^3 1-position, $J(1-3) = 2.1$ Hz), 1.50 (s, 3H, CH_3 2-position), 0.04 (s, 9H, $Si(CH_3)_3$)).

4.13. Synthesis of 1-trimethylsilyl-3-ethylindene

The method of preparation was the same as that for 1-trimethylsilyl-3-methylindene except that 27.1 ml (0.035 mol) of *n*-butyllithium was added to 5.0 g (0.035 mol) of 1-ethylindene. The crude product was obtained as a yellow oil (5.46 g, 72%) which was further purified by distillation at 82–83 °C/0.001 mm Hg to give a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.45–6.98 (m, 4H, arom.), 6.24 (m, 1H sp^2 2-position, $J(2-1) = 1.6$ Hz, $J(2-CH_2) = 1.5$ Hz), 3.31 (m, 1H, sp^3 1-position, $J(1-2) = 1.6$ Hz, $J(1-CH_2) = 2.0$ Hz), 2.58 (q of m, 2H, CH_2, $J(CH_2-CH_3) = 7.5$ Hz, $J(CH_2-2) = 1.5$ Hz, $J(CH_2-1) = 2.0$ Hz), 1.23 (t, 3H, CH_3, $J(CH_3-CH_2) = 7.5$ Hz), −0.14 (s, 9H, $Si(CH_3)_3$).

4.14. Synthesis of 1-trimethylsilyl-3-tert-butylindene

The method of preparation was the same as that for 1-trimethylsilyl-3-methylindene except that 17.6 ml (0.028 mol) of 1.6 M *n*-butyllithium was added to 5.0 g (0.029 mol) of 1-*tert*-butylindene. The crude product was obtained as a yellow oil (5.1 g, 74%) which was further purified by distillation at 90–93 °C/0.001 mm Hg to give a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.9–7.2 (m, 4H, arom.), 6.40 (d, 1H, sp^2 2-position, $J(2-1) = 2.0$ Hz), 3.43 (d, 1H, sp^3 1-position, $J(1-2) = 2.0$ Hz), 1.50 (s, 9H, $3CH_3$), 0.04 (s, 9H, $Si(CH_3)_3$).

4.15. Synthesis of 1,3-bis(trimethylsilyl)indene

The method of preparation was the same as that for 1-trimethylsilyl-3-methylindene except that 16.3 ml (0.026 mol) of *n*-butyllithium was added to 5.0 g (0.026 mol) of 1-trimethylsilylindene. The crude product was obtained as a yellow oil (5.8 g, 85%) which was further purified by distillation at 95–97 °C/0.001 mm Hg to give a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.55–7.33 (m, 2H, arom.), 7.18–7.07 (m, 2H, arom.), 6.76 (d, 1H, sp^2 2-position, $J(2-1) = 1.8$ Hz), 3.52 (d, 1H, sp^3 1-position, $J(1-2) = 1.8$ Hz), 0.24 (s, 9H, $Si(CH_3)_3$ 3-position), −0.15 (s, 9H, $Si(CH_3)_3$ 1-position).

4.16. Synthesis of 1-trimethylsilyl-3-(methylthio)indene

The method of preparation of 1-trimethylsilyl-3-(methylthio)indene was the same as that for 1-trimethylsilyl-3-methylindene except that 18.8 ml (0.031 mol) of 1.6 M *n*-butyllithium was added to 5.0 g (0.031 mol) of 3-(methylthio)indene. The crude product was obtained as a yellow oil (5.10 g, 70%) which was further purified by distillation at reduced pressure (98–100 °C/0.001 mm Hg). ^{1}H NMR ($CDCl_3$): δ 7.60–7.15 (m, 4H, arom.), 6.30 (d, 1H, sp^2 2-position, $J(2-1) = 2.2$ Hz), 3.51 (d, 1H, sp^3 1-position, $J(1-2) = 2.2$ Hz), 2.02 (s, 3H, SCH_3), −0.14 (s, 9H, $Si(CH_3)_3$).

4.17. Synthesis of indenyltrichlorotitanium

$TiCl_4$ (6.4 ml, 0.058 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-Trimethylsilylindene (10.0 g, 0.053 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 a minimum volume of CH_2Cl_2 afforded 13.85 g (97%) of dark red crystals. The dried crystals were sublimed at 80 °C/0.001 mm Hg. ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 2H, arom.), 7.55 (m, 2H,

arom.), 7.19 (d, 2H, 1&3 positions, $J(1-2) = J(3-2) =$ 12 Hz), 7.16 (t, 1H, 2-position, $J(2-1) = J(2-3) = 12$ Hz). Anal. Found: C, 40.18; H, 2.61. $C_9H_7Cl_3Ti$. Calc.: C, 40.12; H, 2.62%.

4.18. Synthesis of 1-methylindenyltrichlorotitanium

The method of preparation was the same as that for indenyltrichlorotitanium except that 5.42 g (0.027 mol) of 1-trimethylsilyl-3-methylindene was added to 3.2 ml (0.027 mol) of $TiCl_4$. The dark-red crystalline product was obtained in 94% yield (7.17 g). ^1H NMR ($CDCl_3$): δ 7.80–7.33 (m, 2H, arom.), 7.60 (m, 2H, arom.), 7.13 (d, 1H, 3-position, $J(3-2) = 3.3$ Hz), 6.93 (d, 1H, 2-position, $J(2-3) = 3.3$ Hz), 2.76 (s, 3H, CH_3). Anal. Found: C, 42.53; H, 3.35. $C_{10}H_9Cl_3Ti$. Calc.: C, 42.38; H, 3.20%.

4.19. Synthesis of 2-methylindenyltrichlorotitanium

The method of preparation was the same as that for indenyltrichlorotitanium except that 5.32 g of 1-trimethylsilyl-2-methylindene (0.26 mol) was added to 3.2 ml (0.029 mol) of $TiCl_4$. The dark-red crystalline product was obtained in 98% yield (7.29 g). Further purification was effected by recrystallization from CH_2Cl_2 and subsequent sublimation at 90 °C/0.001 mm Hg. ^1H NMR ($CDCl_3$): δ 7.73 (m, 2H, arom.), 7.47 (m, 2H, arom.), 7.01 (s, 2H, 1- and 3-positions), 2.62 (s, 3H, CH_3). Anal. Found: C, 42.58; H, 3.19. $C_{10}H_9Cl_3Ti$. Calc.: C, 42.38; H, 3.20%.

4.20. Synthesis of 1-ethylindenyltrichlorotitanium

The method of preparation was the same as that for indenyltrichlorotitanium except that 6.08 g of 1-trimethylsilyl-3-ethylindene (0.028 mol) was added to 3.2 ml (0.029 mol) of $TiCl_4$. The dark-red crystalline product was obtained in 96% yield (7.93 g). Further purification was effected by sublimation at 110 °C/0.001 mm Hg. ^1H NMR ($CDCl_3$): δ7.79 (m, 2H, arom.), 7.51 (m, 2H, arom.), 7.13 (d, 1H, 3-position, $J(3-2) = 3.4$ Hz), 7.00 (d, 1H, 2-position, $J(2-3) = 3.4$ Hz), 3.21 (q, 2H, CH_2, $J(CH_2-CH_3) = 7.4$ Hz), 1.42 (t, 3H, CH_3, $J(CH_3-CH_2) = 7.4$ Hz). Anal. Found: C, 44.54; H, 3.73. $C_{11}H_{11}Cl_3Ti$. Calc.: C, 44.42; H, 3.72%.

4.21. Synthesis of 1-tert-butylindenyltrichlorotitanium

The method of preparation was the same as that for indenyltrichlorotitanium except that 6.74 g of 1-trimethyl-3-*tert*-butylindene (0.028 mol) was added to 3.2 ml (0.029 mol) of $TiCl_4$. The dark-red crystalline product was obtained in 91% yield (8.26 g). Further purification was effected by sublimation at 110 °C/0.001 mm Hg. ^1H NMR ($CDCl_3$): δ 8.1–7.7 (m, 2H, arom.), 7.65–7.35 (m, 2H, arom.), 7.16 (d, 1H, 3-position, $J(3-2) = 3.0$ Hz), 7.04 (d, 1H, 2-position, $J(2-3) = 3.0$ Hz), 1.59 (s, 9H, $3CH_3$). Anal. Found: C, 47.75; H, 4.70. $C_{13}H_{15}Cl_3Ti$. Calc.: C, 47.97; H, 4.65%.

4.22. Synthesis of 1-trimethylsilylindenyltrichlorotitanium

The method of preparation was the same as that for indenyltrichlorotitanium except that 7.07 g (0.027 mol) of 1,3-bis(trimethylsilyl)indene was added to 3.2 ml (0.029 mol) of $TiCl_4$. The dark-red crystalline product was obtained in 97% yield (8.92 g). Further purification was effected by sublimation at 110 °C/0.001 mm Hg. ^1H NMR ($CDCl_3$): δ 7.88 (m, 2H, arom.), 7.54 (m, 2H, arom.), 7.40 (d, 1H, 3-position, $J(3-2) = 0.99$ Hz), 7.26 (d, 1H, 2-position, $J(2-3) = 0.99$ Hz). Anal. Found: C, 42.61; H, 4.48. $C_{12}H_{15}Cl_3SiTi$. Calc.: C, 42.19; H, 4.43%.

4.23. Synthesis of 1-(thiomethyl)indenyltrichlorotitanium

$TiCl_4$ (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 fitted with a gas outlet valve connected to a mercury overpressure bubbler. 1-Trimethylsilyl-3-(thiomethyl)indene (6.58 g, 0.028 mol) was added dropwise and the dark green solution was allowed to react overnight at room temperature. After the solvent was removed under vacuum, the brown-green residue was extracted with 100 ml of toluene. The extracts were transferred via a filter cannula to a 200 ml Schlenk tube, and were concentrated to ca. 50 ml. The green concentrate was then eluted with toluene through Biobeads to yield a blue-green band and a second yellow band. The blue-green solution was concentrated and cooled to −20 °C. Blue-green needles were formed, removed from the supernatant liquid and dried under vacuum (4.06 g, 46%). ^1H NMR ($CDCl_3$): δ 7.68 (m, 2H, arom.), 7.49 (m, 2H, arom.), 7.03 (d, 1H, 3-position, $J(3-2) = 3.4$ Hz), 6.87 (d, 1H, 2-position, $J(2-3) = 3.4$ Hz), 2.80 (s, 3H, CH_3). Anal. Found: C, 38.17; H, 3.05. $C_{10}H_9Cl_3STi$. Calc.: C, 38.07; H, 2.88%.

4.24. Synthesis of 4,5,6,7-tetrahydroindenyltrichlorotitanium

A burgundy-colored solution of 3.0 g (0.011 mol) of indenyltrichlorotitanium in 100 ml of CH_2Cl_2 and 0.227 g (0.001 mol) of PtO_2 were sealed under argon in a 250 ml stainless steel Parr reactor with a glass liner and fitted with a mechanical stirrer. The reaction mixture was pressured with H_2 to 800 psig and allowed to react for 15 h. The orange solution was removed, concentrated, and chilled to −20 °C. Orange crystals (3.01 g,

100%) were isolated and dried under vacuum. ^{1}H NMR ($CDCl_3$): δ 7.05 (t, 1H, 2-position, $J(2-1,3) = 3.2$ Hz), 6.65 (d, 2H, 1- and 3-positions, $J(1,3-2) = 3.2$ Hz), 3.45–2.60 (m, 4H, 5- and 6-positions), 2.15–1.55 (m, 4H, 4- and 7-positions). Anal. Found: C, 39.46; H, 4.03. $C_9H_{11}Cl_3Ti$. Calc.: C, 39.53; H, 4.05%.

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