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Electronic effects of bis(2-aryl-4,5,6,7-tetrahydroindenyl)titanocene dichlorides on the catalytic epoxidation of *trans*-3-hexene

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Abstract

The catalytic epoxidation of *trans*-3-hexene with electronically different bis(2-aryl-4,5,6,7-tetrahydroindenyl)titanium dichloride complexes in the presence of stoichiometric tert-butylhydroperoxide has been studied. The results show that both electron donating (4-methoxyphenyl and 4-methylphenyl) and withdrawing (4-bromophenyl) groups on the 2-position of 4,5,6,7-tetrahydroindene produce an enhancement in the number of turnovers of epoxide formed during 15 h at 80°C when compared to the 2-phenyl substituted complex. The facile preparation and purification of these previously unreported ligands and the corresponding titanocene complexes, and the results of the catalytic epoxidation of *trans*-3-hexene are described.

Key words: Titanium; Metallocenes; Catalysis; Epoxidation

1. Introduction

While both the mechanism and the synthetic applications of the asymmetric epoxidation of functionalized alkenes catalyzed by titanium complexes in the presence of tert-butylhydroperoxide have been extensively studied [1], neither the mechanism nor the synthetic applications of asymmetric titanocene-catalyzed epoxidation of unfunctionalized alkenes have been well-studied. We recently reported the only example of an asymmetric epoxidation of unfunctionalized alkenes using a chiral titanocene complex [2]. Although the ability of polymer-supported titanocene complexes to catalyze the epoxidation of unfunctionalized alkenes was first reported [3] in 1981, no mechanistic details concerning this potentially synthetically useful titanocene-catalyzed epoxidation have been reported. In order to better understand this catalytic process and thereby aid our quest for developing more stereoselective catalysts, we undertook a mechanistic study of the titanocene-catalyzed epoxidation of unfunctionalized alkenes. As a starting point in addressing this mechanistic problem, we report here a study of how varying the electronic nature of the cyclopentadienyl ligands in titanocene dichlorides effects the rate of catalyst turnover in the epoxidation of *trans*-3-hexene.

2. Results

2.1. Metallocene synthesis

To study the effects of varying the electronic nature of the cyclopentadienyl ligands in titanocene-catalyzed epoxidations, we synthesized a series of structurally and sterically similar, but electronically different 2-aryl-4,5,6,7-tetrahydroindenyl ligands **3a–d** and converted them to the titanocene dichlorides **5a–d** as shown in Scheme 1. The phenyllithium or Grignard reagents **2a–d** derived from 1-bromo-4-methoxybenzene, 1-bromo-4-methylbenzene, bromobenzene and 1,4-dibromobenzene were added to the known bicyclo[4.3.0]non-6-en-8-one **1** [4] in the presence of $CeCl_3$ [5] to yield cyclopentenols **4a–d**. These unpurified and unstable allylic alcohols underwent elimination in the presence of *p*-TsOH to provide the desired 2-aryl-4,5,6,7-tetrahydroindenyl ligands **3a–d**. Following standard metalation procedures [6], the lithium salts of ligands **3a–d** were reacted with $TiCl_3$ in THF which gave after oxidation with air and HCl the metallocene catalysts **5a–d** in good yield. We were unsuc-

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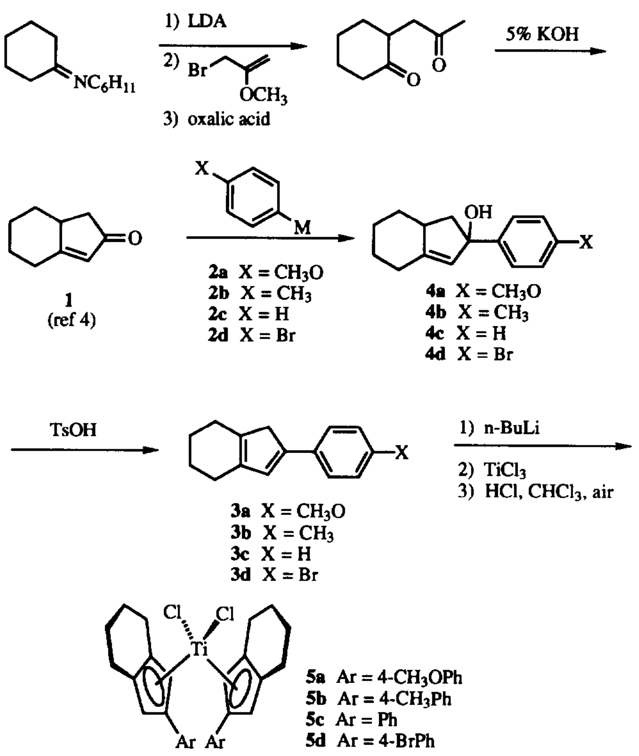


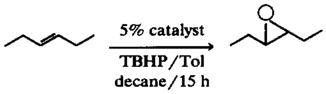
Scheme 1. Synthesis of titanocene dichloride catalysts **5a–d**.

cessful in metalating the analogous 2-arylindenyl ligands and were unable to add the Grignard reagent from 1-bromo-4-trifluoromethylbenzene to cyclopentenone **1**.

2.2. *Catalytic epoxidation of trans-3-hexene*

For each of the four titanocene complexes, we combined *trans*-3-hexene, 5% of the catalyst precursor **5a–d**, excess tert-butylhydroperoxide and n-decane (internal standard) in toluene at room temperature under nitrogen [2]. As evidenced by the lack of a color change, no perceptible reaction occurred until the reaction mixtures were heated. Within 1 h at 80°C, each of the purple-red solutions became pale yellow and heating was continued at 80°C for 15 h. The reaction mixtures were then analyzed by capillary gas chromatography [2]. The range of catalytic activity as measured by the equivalents of *trans*-3-hexene oxide produced per equivalent of titanocene complex is summarized in Table 1. In a control reaction, no epoxidation occurred at 80°C in the absence of titanocenes **5a–5d**. Complex **5a** containing the electron donating methoxy substituent had a turnover number twice that of the parent complex **5c** and the methyl substituted complex **5b**. Complex **5d**, containing the electron-withdrawing bromo-substituent, had a three-fold increase in the number of turnovers relative to **5c**.

TABLE 1. Catalytic epoxidation of *trans*-3-hexene



catalyst	temperature (°C)	time (h)	number of Turnovers
5a (X = OCH_3)	80	15	15
5b (X = CH_3)	80	15	4
5c (X = H)	80	15	6
5d (X = Br)	80	15	25

3. Discussion

In order for a titanocene complex to function as a catalyst for the epoxidation reaction, the formation of insoluble and catalytically inactive oligomeric μ-oxotitanium complexes must be prevented [7]. In the past, oligomer formation has been prevented by either supporting the metallocene at low loading on a polymer backbone [3], or by hindering intermetallocene interactions by having sterically encumbered chiral titanocene complexes [2,8]. We have chosen sterically hindered bis(2-aryltetrahydroindenyl)titanium complexes as models of sterically encumbered chiral titanocenes since they should not be prone to formation of oligomeric μ-oxotitanium complexes. By locating an electronically variable substituent at the 4-position of the phenyl group we tried to minimize any steric differences and maximize electronic differences between the analogous titanocene dichlorides **5a–d**.

The most intriguing result in this study is that both electron donating and electron withdrawing substituents (based on σ_p values) on the tetrahydroindenyl ligands promote a higher number of turnovers per hour. When the turnover number per 15 h is plotted against σ_I, however, a linear relationship is observed with the most electron withdrawing substituents giving the greatest number of turnovers. The explanation of this result could either be attributed to increased catalyst lifetime or an increased rate of catalytic turnovers. Initial attempts to distinguish these possibilities have not been successful; initial rates are not reproducible, presumably due to variable induction periods. The identity of the catalytically active species formed at 80°C from the titanocene complexes **5a–5d** in the presence of tert-butylhydroperoxide has not been determined; attempts at isolating metallocene species from the reaction mixture have been unsuccessful. We envision the catalytic cycle proceeding through incorporation of the oxidant into the metal complex followed by transfer of an oxygen to the alkene. If the rate determining step involved electrophilic transfer of an oxygen atom from the metal complex to the alkene, then an increase in the reactivity and number of turnovers would be expected as the organometallic species became more electron poor—as we observe based on the σ_I values of our substituents. Collins has recently reported analogous findings in the lowering of activity in the polymerization of alkenes with metallocene catalysts containing either electron donating or electron withdrawing substituents [9].

4. Conclusion

In conclusion, we have developed efficient syntheses of new 2-aryl-4,5,6,7-tetrahydroindenyl ligands which contain sterically similar but electronically different phenyl substituents. We have demonstrated that titanocene dichloride complexes containing these ligands can promote the catalytic epoxidation of *trans*-3-hexene in the presence of tert-butylhydroperoxide and that the electronic nature of the ligands significantly changes the catalytic activity.

5. Experimental section

5.1. General

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. All ^{1}H NMR spectra were obtained using a Varian XL-300. Infrared spectra were recorded on a Bio-Rad FTS-7 FT-IR with a dedicated Bio-Rad 3240-SPC computer. Low-resolution mass spectra (reported as m/z (relative intensity at 12, 40 or 70 eV) were recorded on either a Finnegan MAT-90 or a Hewlett Packard 5985 instrument. Gas chromatography was performed on a Hewlett Packard 5890A gas chromatograph equipped with an achiral Hewlett Packard fused silica capillary column (no. 19091j-102, 25 m × 0.02 mm i.d., 0.33 mm film of SE-30). Response factors for olefins and epoxides in decane were determined as described by Colletti [10]. Solvents were distilled under nitrogen from standard drying reagents. All reactions involving air or moisture sensitive species were performed under argon utilizing Schlenk techniques or a Vacuum Atmospheres Dri-Box under a nitrogen atmosphere. All degassed solvents and reaction mixtures were prepared via three freeze-pump-thaw cycles conducted under argon on a Schlenk line at < 0.001 mm Hg. Anhydrous tert-butylhydroperoxide in toluene (3.96 M) was prepared as described by Sharpless [11]. The following compounds were prepared by literature methods: Bicyclo[4.3.0]non-6-ene-8-one (**1**) [4], (4-methylphenyl)magnesium bromide (**2b**) [12], and (4-bromophenyl) magnesium bromide (**2d**) [13]. The preparation of (4-methoxyphenyl)magnesium bromide (**3a**) is described below. Elemental analyses were performed by Desert Analytics, Tucson, AZ, USA.

5.2. Synthesis of (4-Methoxyphenyl)magnesium bromide (2a)

To a 200 ml, two-neck round bottom flask equipped with a condenser and charged with magnesium turnings (2 equiv) under nitrogen was added anhydrous THF to make a 0.5 M solution of the resulting Grignard reagent. 4-Methoxy-1-bromobenzene (1 equiv) was added slowly via syringe at a sufficient rate to maintain a gentle reflux. After the solution ceased to reflux on its own, the solution was heated under reflux for one hour and cooled. The solution (assumed to be 0.5 M in Grignard) was decanted by cannula off of the excess magnesium and was used directly in the next reaction.

5.3. 2-Phenyl-4,5,6,7-tetrahydroindene (3c): representative synthesis of 2-aryltetrahydroindenes

To a −50°C THF solution of $CeCl_3$ (0.910 g, 3.69 mmol) which had been previously stirred at room temperature for at least three hours was added phenyllithium (1.8 M in hexane, 1.0 ml, 1.8 mmol) via syringe over fifteen minutes (phenylmagnesium bromide works as well). The solution was stirred for 0.5 h at −20°C before the addition of bicyclo[4.3.0]non-6-en-8-one (**1**) (0.250 g, 1.8 mmol) at −78°C. After one hour the slurry was allowed to come to room temperature and stirred for one additional hour. The solution was quenched at 0°C with saturated NH_4Cl and the organic phase extracted with diethyl ether, brine, dried over $MgSO_4$ and concentrated. The crude alcohol was eliminated at room temperature in benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid. The crude product was purified by flash chromatography (SiO_2, petroleum ether) to yield **3c** as a white crystalline solid (0.130 g, 0.66 mmol) in 36% yield, mp 65–68°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (m, 4H), 2.29–2.39 (m, 4H), 3.21 (s, 2H), 6.65 (s, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 2H), 7.42 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.90, 137.7, 135.76, 132.90, 129.20, 128.78, 127.50, 125.55, 124.33, 116.61, 43.13, 25.48, 24.40, 23.20, 23.01; IR (thin film) 2937, 2361, 2333, 1720, 1558, 1454 cm^{-1}; MS, m/z (70 eV, rel intensity) 196 (M^+, 100), 168 (50), 153 (17), 105 (17).

5.4. 2-(4-methoxyphenyl)-4,5,6,7-tetrahydroindene (3a)

Following the representative procedure for the synthesis of 2-aryltetrahydroindenes above but using (4-methoxyphenyl)magnesium bromide (**2a**) (11 mmol) and cyclopentenone **1** (1.00 g, 7.41 mmol), **3a** was obtained

(0.903 g) in 58% yield as a white solid, mp 117–118°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (m, 4H), 2.61–2.70 (m, 4H), 3.41 (s, 2H), 3.85 (s, 3H), 6.55 (s 1H), 6.90 (d, 2H, $J = 8.0$ Hz), 7.45 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.33, 149.02, 134.35, 129.43, 127.66, 126.98, 125.77, 113.97, 113.51, 111.65, 55.30, 43.29, 25.47, 24.46, 23.31, 23.10; IR (thin film) 3052, 2984, 2930, 2835, 2361, 2304, 1504, 1419, 1264 cm^{-1}; MS, m/z (70 eV, rel intensity) 226 (M^+, 100), 198 (52).

5.5. *2-(4-methylphenyl)-4,5,6,7-tetrahydroindene (3b)*

Following the representative procedure for the synthesis of 2-aryltetrahydroindenes above but using (4-methylphenyl)magnesium bromide (**2b**) (14.7 mmol) and cyclopentenone **1** (1.00 g, 7.41 mmol), **3b** was obtained (0.552 g) in 48% yield as a white solid, mp 76–78°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (m, 4H), 2.22 (s, 3H), 2.30–2.38 (m, 4H), 3.21 (s, 2H), 6.60 (s, 1H), 7.09 (d, 2H, $J = 8.0$ Hz), 7.31 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.22, 138.88, 138.66, 135.70, 133.92, 129.18, 129.06, 128.61, 125.42, 124.53, 115.61, 43.12, 25.48, 24.43, 23.26, 23.06; IR (thin film) 3053, 2938, 2361, 2333, 1698, 1650, 1557, 1455, 1264 cm^{-1}; MS, m/z (70 eV, rel intensity) 210 (M^+, 100), 182 (38), 167 (43).

5.6. *2-(4-bromophenyl)-4,5,6,7-tetrahydroindene (3d)*

Following the representative procedure for the synthesis of 2-aryltetrahydroindenes above but using (4-bromophenyl) magnesium bromide (**2d**) (11 mmol) and cyclopentenone **1** (1.00 g, 7.41 mmol), **3d** was obtained (0.304 g) in 15% yield as a white flaky solid, mp 128–131°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (m, 4H), 2.30–2.39 (m, 4H), 3.21 (s, 2H), 6.67 (s, 1H), 7.31 (d, 2H, $J = 8.5$ Hz), 7.40 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.92, 139.87, 139.05, 131.89, 131.56, 130.31, 128.53, 126.12, 199.52, 43.14, 25.54, 24.39, 23.20, 23.02; IR (thin film) 2931, 2857, 2361, 2333, 1697, 1651, 1567, 1539, 1261, 1093, 1018 cm^{-1}; MS, m/z (70 eV, rel intensity) 276 (M^{+2}, 89), 275 (M^{+1}, 20), 246 (33), 195 (25).

5.7. *Bis(2-phenyl-4,5,6,7-tetrahydroindenyl)dichlorotitanium (5c): representative synthesis of titanocene dichlorides*

To a 10 ml two-neck pear-shaped flask equipped with a vacuum adapter and charged with 2-phenyl-4,5,6,7-tetrahydroindene (**3c**) (0.200 g, 1.0 mmol) was added THF (3 ml). After the colorless solution was cooled to −78°C, n-butyl lithium (1.30 M, 0.82 ml, 1.07 mmol) was added dropwise via syringe to achieve a bright yellow color which upon gradual warming to 0°C became deep red. After stirring for 30 min at 0°C, the solution was recooled to −78°C and transferred to a previously cooled (−78°C) solution of $TiCl_3$ (0.074 g, 0.48 mmol) in THF (1 ml) to achieve a dark purple brown color. The solution was gradually warmed to room temperature and then refluxed for 6 h. The solvent was removed *in vacuo*, the residue taken up in $CHCl_3$ (2 ml) and 6 M HCl (2 ml) added and allowed to stir for 2 h. The organic layer was separated and the water layer extracted twice with CH_2Cl_2, dried over $CaCl_3$ and concentrated to reveal a dark purple solid. The solid was taken up in CH_2Cl_2 and the crystals precipitated with distilled hexanes, filtered and dried *in vacuo* to give **5c** (0.239 g) in 46% yield as a dark purple crystalline solid, mp. 91–92°C. Anal. Calc. for $C_{30}H_{30}TiCl_2$-H_2O: C 68.33, H 6.12; found: C 68.65, H 5.88%. ^{1}H NMR (300 MHz, $CDCl_3$) d 1.31–1.50 (m, 2H), 1.80–2.05 (m, 2H), 2.15–2.35 (m, 2H), 2.34–2.54 (m, 2H), 6.40 (s, 2H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 2H), 7.42 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.90, 134.00, 128.95, 127.72, 127.69, 125.45, 119.96, 92.907, 24.71, 21.83; IR (thin film) 3053, 2984, 2683, 2360, 2304, 1682, 1650, 1420, 1264; MS, m/z (70eV, rel intensity) 508 (M^+, 100), 473 (89) 436 (96).

5.8. *Bis[2-(4-methoxyphenyl)-4,5,6,7-tetrahydroindenyl]-dichlorotitanium (5a)*

Following the representative procedure for the synthesis of titanocene dichlorides above but using 2-(4-methoxyphenyl)-4,5,6,7-tetrahydroindene (**3a**) (0.156 g, 0.69 mmol), n-BuLi (1.30 M in hexanes, 0.55 ml, 0.72 mmol) and $TiCl_3$ (0.053 g, 0.345 mmol), **5a** was obtained (0.185 g) in 47% yield as a purple crystalline solid, mp 174°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39–1.42 (m, 2H), 1.85–1.90 (m, 2H), 2.21–2.23 (m, 2H), 2.43–2.59 (m, 2H), 3.82 (s, 3H), 6.43 (s, 2H), 6.85 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.23, 135.25, 127.07, 126.85, 118.98, 114.15, 114.05, 55.38, 24.84, 21.89; IR (thin film) 3052, 2985, 2361, 2305, 1697, 1650, 1557, 1433, 1420, 1264 cm^{-1}; MS, m/z (FAB, rel intensity) 570 (M^{+1}, 4), 569 (M^+, 3), 533 (31), 225 (100).

5.9. *Bis[2-(4-methylphenyl)-4,5,6,7-tetrahydroindenyl]dichlorotitanium (5b)*

Following the representative procedure for the synthesis of titanocene dichlorides above using 2-(4-methylphenyl)-4,5,6,7-tetrahydroindene (**3b**) (0.120 g, 0.57 mmol), n-BuLi (1.30 M in hexanes, 0.46 ml, 0.60 mmol) and $TiCl_3$ (0.044 g, 0.29 mmol), **5b** was obtained (0.138 g) in 45% yield as a dark purple crystalline solid, mp 97–100°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39–1.45 (m, 2H), 1.85–1.91 (m, 2H), 2.18–2.20 (m, 2H), 2.38–2.50 (m, 2H), 6.43 (s, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

137.58, 135.43, 131.50, 129.53, 129.44, 127.75, 125.38, 119.71, 24.74, 21.31; IR (thin film) 3051, 2983, 2303, 1420, 1264, 1016 cm^{-1}; MS, *m/z* (FAB, rel intensity) 537 (M$^+$, 1), 501 (11), 209 (45).

5.10. Bis[2-(4-bromophenyl)-4,5,6,7-tetrahydroindenyl]-dichlorotitanium (5d)

Following the representative procedure for the synthesis of titanocene dichlorides above using 2-(4-bromophenyl)-4,5,6,7-tetrahydroindene (**3d**) (0.150 g, 0.555 mmol), KH (35%, 70 mg, 0.61 mmol) and TiCl$_3$ (0.043 g, 0.28 mmol), **5d** was obtained (0.130 g) in 35% yield as a dark purple/red crystalline solid, mp 219°C. ^{1}H NMR (300 mHz, CDCl$_3$) d 1.48–1.53 (m, 2H), 1.89–1.94 (m, 2H), 2.37–2.43 (m, 2H), 2.56–2.60 (m, 2H), 6.44 (s, 2H), 7.19 (d, 2H, $J = 8.4$ Hz), 7.45 (d, 2H, $J = 8.4$ Hz); ^{13}C NMR (75 MHz, CDCl$_3$) d 136.13, 132.89, 131.91, 127.04, 126.38, 121.69, 119.16, 24.97, 21.80; IR (thin film) 3051, 2982, 2939, 2361, 2333, 1697, 1650, 1557, 1485, 1264 cm^{-1}; MS, *m/z* (70 eV, rel intensity) 666 (M$^+$, 9), 631 (45), 273 (89).

5.11. Catalytic epoxidation using titanocene dichlorides

All reactions were run under an inert atmosphere with dry, distilled and degassed reagents. In a dry box, an oven-dried round bottom flask containing a flea stirbar was charged with 5% catalyst (5.0 mg, 7.5×10^{-3} mmol), *trans*-3-hexene (0.21 g, 2.5 mmol, 332 equiv), decane (16.0 mg, 0.112 mmol, 50 equiv), and tert-butylhydroperoxide (3.96 M in toluene, 0.63 ml, 2.5 mmol, 332 equiv), respectively. A 10 μl aliquot was removed and transferred to another sealed vial, diluted with 25 μl of toluene and analyzed by GC. The reaction flask was sealed with a greased ground-glass stopper and heated to 80°C for 15 h. The cooled faint yellow reaction mixture was then analyzed by GC on a 25 m X 0.02 mm i.d. fused silica column with a 0.33 mm film of SE-30 under the following conditions:

Temperature Programming	Retention Time
initial, ramp, final (°C/min)	olefin, epoxide, decane
70/3, 10/1, 130/1	2.14, 3.28, 7.70 @ 15 psi

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