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Competitive intramolecular Ti–C versus Al–C alkene insertions: examining the role of Lewis acid cocatalysts in Ziegler–Natta alkene insertion and chain transfer reactions

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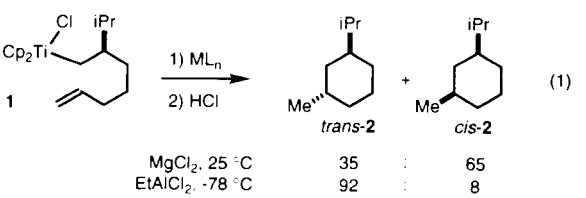
Abstract

Mechanistic aspects of Ziegler–Natta olefin insertion, which include catalyst/cocatalyst interactions, chain propagation, and chain termination, have been examined for systems which model the $Cp_2Ti(Cl)R/RAlCl_2$ and $Cp_2Ti(Cl)R/MgX_2$ catalyst complexes. The reaction of (2-butyl-6-hepten-1-yl)titanocene chloride with (2-propyl-6-hepten-1-yl)aluminum dichloride : diethyl etherate produced 78% cyclization of the titanocene ligand, while less than 2% of the ligand originating on aluminum cyclized. In a complementary experiment, the reaction of (2-propyl-6-hepten-1-yl)titanocene chloride and (2-butyl-6-hepten-1-yl)aluminum dichloride : diethyl etherate again produced only intramolecular insertion of the titanium ligand (58%). Based on these results, equilibration of ligands through transmetallation between titanium and aluminum did not occur under these reaction conditions, and selective insertion into the titanium–carbon bond was confirmed for this process. Similarly, ligand cyclization with $Cp_2Ti(Cl)R/MgX_2$ also occurred through insertion into the titanium–carbon bond. The product distribution generated by the MgX_2 was highly solvent dependent. Cyclization in CH_2Cl_2 was very efficient, while reaction in toluene generated numerous products. Included in the toluene reaction mixture were compounds that resulted from ligand transposition/chain transfer of the titanium ligand.

Keywords: Titanium; Aluminium; Magnesium; Olefin insertion; Ziegler–Natta catalysts; Chain transfer

1. Introduction

In previous studies of intramolecular alkene insertion into titanium–carbon bonds, substitution on the alkyl tether resulted in the stereoselective formation of cyclopentane [1] and cyclohexane products (Eq. (1)) [2]. These systems, which are active polymerization catalyst/cocatalyst complexes and model the olefin insertion step in Ziegler–Natta processes [3], revealed a dependence of the stereoselective cyclization of **1** to **2** on the Lewis acid additive and reaction temperature. While treatment of **1** with MgX_2 at 25°C produced a 35:65 ratio of *trans*-**2**/*cis*-**2**, the use of $EtAlCl_2$ at −78°C generated a significantly different ratio (92:8) of *trans*-**2**/*cis*-**2** [2]. The use of methylaluminoxane ($[-O-Al(Me)-]_n$, MAO), a widely used Ziegler–Natta polymerization cocatalyst, generated the same product ratio as that observed for $EtAlCl_2$ at −45°C when cyclization of a similar substrate was examined. With the most apparent variation in the Lewis acids centered around the different metal center, the nature of the titanium–ligand–cocatalyst interactions was important to the stereoselective ring formation.



Transition metal–ligand–cocatalyst interactions have been structurally characterized in several cases related to Ziegler–Natta polymerization systems, and reflect the character of the electron deficient zirconocene [4] or titanocene centers [5]. Of particular interest were

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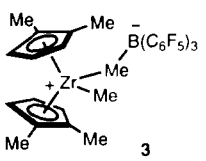
complexes that bridged alkyl ligands between two electron deficient metal centers. Compound **3**, an active ethylene and propylene polymerization catalyst, has a methyl substituent bridging between the zirconium cation and the boron-centered counterion [6]. Alkyl substituents such as methyl [7] and ethylene (**4**) [8] have also been shown to bridge between two zirconium centers when the transition metal centers were rendered electron deficient by complexation with aluminum. Complex **5**, in which ytterbium is isoelectronic with zirconium in **3**, has methyl substituents that bridge the lanthanide metal and aluminum [9].

With the propensity for zirconium and titanium alkyl groups to bridge and exchange ligands with aluminum complexes [10], ligand cyclization on the Lewis acid additive (magnesium or aluminum) was a potential source of the variation in the observed stereoselectivities. Alternatively, the variation in reaction temperature required by the different cocatalysts could alter the stereoselectivity of the insertions, as has been observed in stereoselective propylene polymerization [11]. In order to heighten our understanding of these intramolecular insertion processes and the various stereochemical outcomes obtained for different Lewis acid cofactors, these systems were studied in greater detail. Features of particular interest in this study include (1) the potential for facile ligand transfer/equilibration, (2) the nature of the catalyst–ligand–cocatalyst interactions, and (3) the possibility of cyclization by insertion with the cocatalyst metal–carbon bond.



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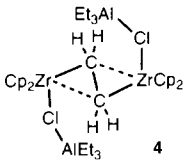

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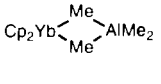

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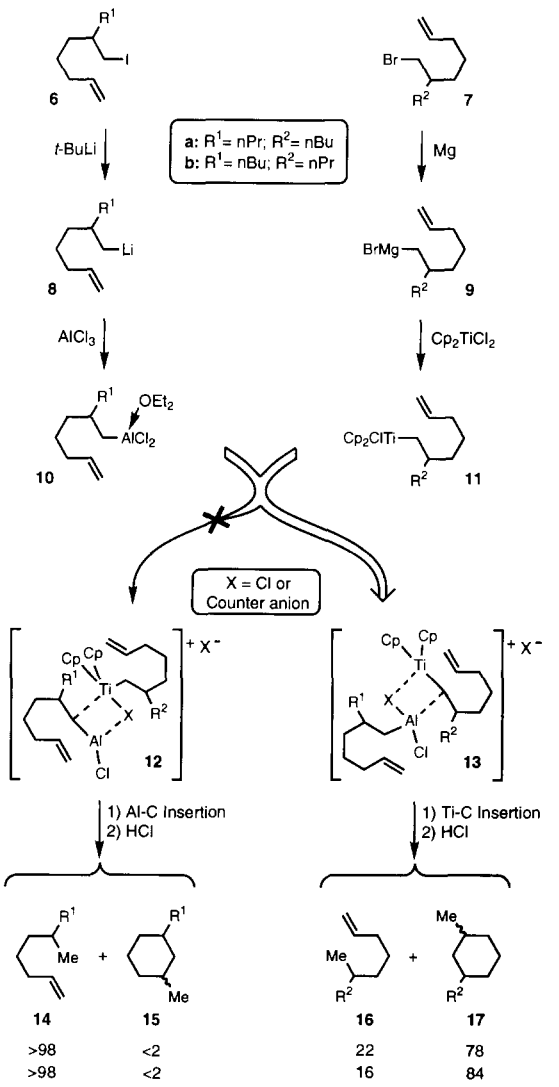
2. Results and discussion

2.1. System design

In order to address the possibility of both ligand exchange and cyclization of the ligand on the aluminum, a system was designed in which the relative reactivity of the Al–C and Ti–C bonds could be determined for the active catalyst/cocatalyst complex rather than the individual organometallic species. Equal opportunity for cyclization of the ligand on titanium and aluminum was provided through the preparation of different alkene substrates tethered to each individual metal. Based on observations that both titanium [2,3] and aluminum [12] tethered alkenes independently cyclize to form six-membered rings, the amounts of ring formation for the ligand on each metal would accurately reflect the relative reactivity of each metal center toward olefin insertion.



In a system analogous to **1**, which models the $Cp_2Ti(Cl)Et/EtAlCl_2$ Ziegler–Natta polymerization system [3,13], 6-hepten-1-yl complexes of titanium and aluminum were prepared for competitive intramolecular insertion. In order to distinguish between cyclization of the ligand on titanium versus that on aluminum, ligands were prepared that differed in the substituent at the carbon β to the metal. The use of *n*-propyl and *n*-butyl substituents were selected to minimize differences in relative rate due to substituent effects, and to model the insertion of an α-olefin into the metal–carbon bond of a growing poly-1-pentene ($R = {}^{n}Pr$) and poly-1-hexene ($R = {}^{n}Bu$) chain $M\text{-}(CH_2CHR)_n\text{-}$Polymer, respectively [2].

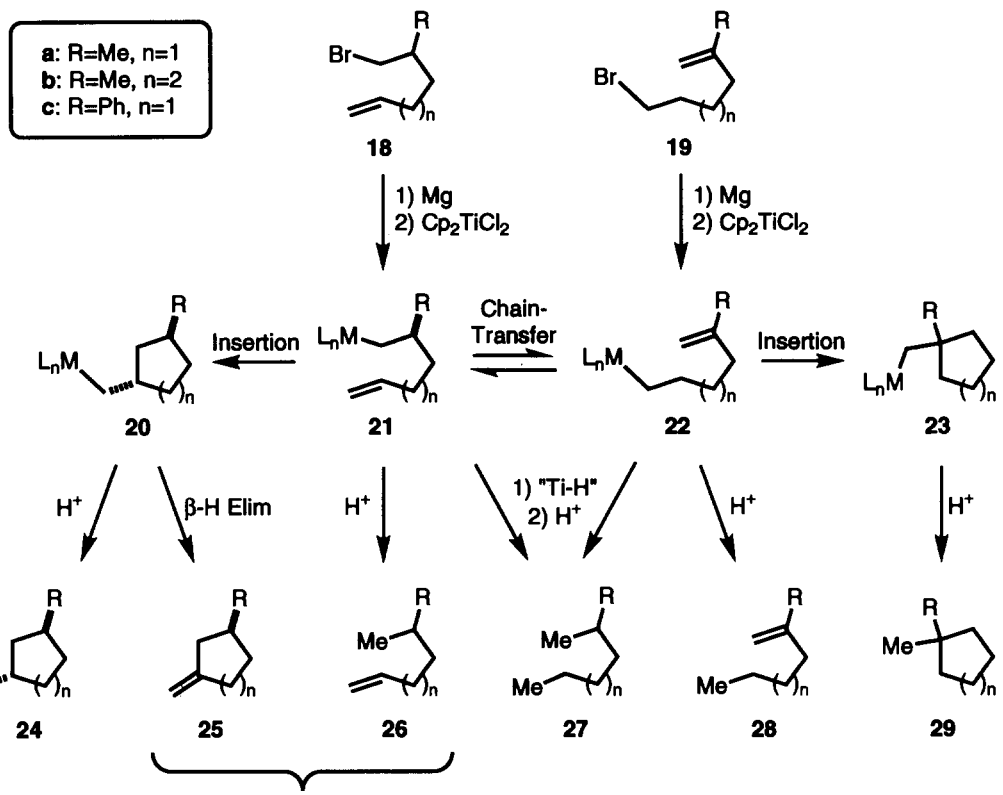
The organometallic complexes were prepared from the corresponding halides **6** and **7**. Preparation of the corresponding Grignard reagent **9** was accomplished by

treatment of **7** with Mg. Transmetallation of the ligand to Cp_2TiCl_2 following established procedures gave the catalyst model **11** [1,2,14]. Lewis acid **10** was generated by metallation of **6** with ^tBuLi to give intermediate **8**, followed by transmetallation to $AlCl_3$ [15]. During formation of **10**, a mixture of Al–I and Al–Cl species was generated as a result of halogen metathesis. However, ligand cyclization did not occur under these conditions, as evidenced by less than 2% formation of **15** upon treatment with HCl. Efforts to remove the coordinated Et_2O from **10**, or to prepare the Al species in non-ethereal solvents, were not successful, but the presence of complexed Et_2O did not prevent the competitive cyclization reactions. Combination of **10** and **11** resulted in a complex which was active toward alkene insertion.

2.2. Competitive cyclization of Ti–R versus Al–R ligands

Direct evidence for selective insertion at the titanium center was obtained through analysis of the product mixtures resulting from the reaction of **10** and **11** at −78°C. The combination of **10a** with **11a** did not produce intramolecular alkene insertion of the ligand originating on aluminum, as evident from the >98:2 ratio of **14a**:**15a**, whereas the titanocene based ligand cyclized to give a 22:78 ratio of **16a**:**17a**. Treatment of the reaction mixture with *N*-bromosuccinimide resulted in the formation of **7b**, which confirmed the presence of **10a** even after selective cyclization of **11a** [16]. Significant variations in cyclization rate due to substituent differences on the alkenyl ligand were negligible, as demonstrated by the complementary reaction of **10b** and **11b**. In this case, intramolecular insertion of the titanium ligand was observed for **11b**, which cyclized to an extent of 84% while **10b** produced <2% ring formation.

An alternative pathway, ligand cyclization through sequential homolysis of the titanium-carbon bond and subsequent radical cyclization, did not occur under these reaction conditions. Although somewhat less selective than the analogous isopropyl derivative **1**, the



18a (0.10 *M*)	67%	*Obscured*		21%	11%	2%
18a (0.25 *M*)	71%	5%		12%	12%	<2%
18a (0.44 *M*)	57%	*Obscured*		18%	21%	4%
18a (0.60 *M*)	54%	*Obscured*		17%	23%	7%
(β-D)**18a** (0.25 *M*)	60%	15%		14%	<2%	<2%
19a (0.25 *M*)	14%	<2%		5%	61%	<2%
18b (0.25 *M*)	61%	13%		12%	12%	2%
18c (0.25 *M*)	45%	24%	4%	10%	8%	<2%

trans-**17a**/*cis*-**17a** ratio produced by the aluminum mediated cyclization was 60:40 [2]. In contrast, radical cyclization of **7a** (Bu_3SnH, AIBN, C_6H_6, 80°C, 0.01 M) produced a reversal of product selectivity to give a 42:58 ratio of *trans*-**17a**/*cis*-**17a** [2].

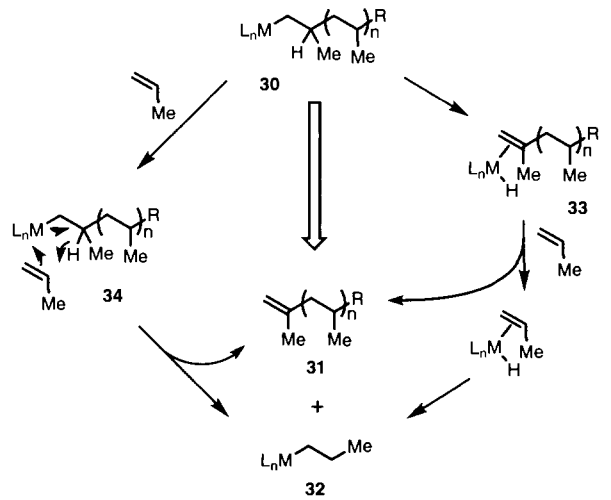
In this system, the aluminum complex activated the alkyl transition metal species for alkene insertion rather than a titanium cocatalyst serving to activate the alkyl aluminum species toward insertion. These results provide further support for the concept that the titanium complex is the active center for polymer chain propagation in this Ziegler–Natta model system. In addition to obtaining direct evidence for preferred chain propagation at titanium, another important feature of the active catalyst/cocatalyst complex became apparent through the combination of **10** and **11** [17]. In contrast to previous proposals [18], insertion into the Al–C bond did not occur, and the rapid equilibration of ligands between the two metals was not observed under these reaction conditions. Thus, if a bridging structure contributed to the active catalyst/cocatalyst mixture, a symmetrically bridging alkyl species was not present, and the active complex is more accurately represented by a structure such as **13** rather than **12**.

2.3. Examination of Ti–R systems promoted by MgX_2

Alternative methods were used to confirm titanium-centered alkene insertion for ligand cyclization in the presence of MgX_2. The reaction of **9** in Et_2O with 1.0 equiv. of Cp_2TiCl_2 in CH_2Cl_2 resulted in 87% cyclization of the ligand, while the addition of only 0.20 equiv. of Cp_2TiCl_2 generated 19% of the cyclic products. In this system, which modeled the $Cp_2TiMe_2/MgCl_2/TiCl_4$ catalyst/cocatalyst mixture [19], the direct relationship was apparent between the amount of Cp_2TiCl_2 added and extent of cyclization. Even though intramolecular five-membered ring formation has been observed for organomagnesium reagents at 60–100°C, the Cp_2TiCl_2 served to promote cyclization of the organomagnesium ligand at ambient temperature [20]. Facile ligand exchange between titanium and magnesium, following initial transmetallation (**9** to **11**), was not observed under these reaction conditions. Although the treatment of **11** with 0.5 equiv. of $EtAlCl_2$ resulted in complete conversion to **17** upon protonolysis, the addition of 1.0 equiv. of $EtAlCl_2$ to **9** did not produce measurable cyclization.

2.4. Observation of chain-transfer processes in MgX_2 promoted cyclization reactions

When transmetallation of the Grignard reagent to Cp_2TiCl_2 was performed in toluene rather than CH_2Cl_2, the typically selective cyclization resulted in the generation of a number of reaction products. These



dramatic solvent effects were examined in greater detail through the use of **18**. Treatment of **18a** with Mg, transmetallation to Cp_2TiCl_2 in toluene, and subsequent protonolysis generated a mixture of five significant products. Analysis of this mixture confirmed the expected stereoselective *trans* formation of **24a** as well as the generation of one or both of **25a** and **26a** (5–15%), which could not be separated through GC analysis. In addition, analysis of the mixture revealed evidence for alkene reduction, either through titanium hydride species (**33**) or reduction through **34**, which were responsible for the formation of products **27a**, **28a**, and **29a** [21].

There are several possible pathways for the formation of **27**, **28**, and **29** through routes related to chain transfer processes in Ziegler–Natta catalyst systems. Involvement of β-H transfer for chain transfer/chain termination steps in titanium-promoted polymerizations have been proposed [22], and recently, there has been a wave of activity to confirm the presence of related processes through end group analysis of polymers. In general, termination of a propagating polymer chain (**30**) has produced terminal olefin **31** and a nascent polymer chain **32**. These products can result from β-hydride elimination to give **33** followed by olefin exchange and subsequent insertion of the monomer. Alternatively, a concerted chain transfer process can be "triggered" by the monomer as illustrated in **34** [23].

A number of reports of chain transfer in Ziegler–Natta processes have appeared. Studies have found that both β-H and β-Me transfers occur in $(CpMe_5)Zr$ systems [23], and in some cases, the β-Me transfer is preferred [24]. Both β-H and β-Me elimination reactions have been observed for the isoelectronic lanthanide catalysts as well [25], and related studies have been used to examine the effects of different sub-

stituents at the β-position related to β-H elimination [26]. Although this process has received significant attention in the polymerization of propylene using zirconium or lanthanide catalysts, titanium catalysts have been the subject of less study, and β-Me elimination has not been observed for Ti species. In addition, the monomer substituent and solvent effects on the propagation versus chain transfer steps (either H or Me) have not been determined for alkene insertion promoted by Lewis acid cocatalysts.

The olefin monomer has been reported to "trigger" both olefin insertion [27] and the intermolecular chain transfer [23] processes in Ziegler–Natta catalysis. Therefore, model systems used to explore the chain transfer process in titanium alkyl complexes were designed with a 1:1 stoichiometry of olefin substrate to transition metal center. For this purpose, the use of **18** allowed the facile examination of the monomeric insertion products through ligand transposition. In this system, transmetallation was expected to form **21a** followed by cyclization to give **20**. Ligand removal, through β-hydride elimination or protonolysis, confirmed the intermediate formation of **20** and **21**. Transformation of **21** to **22** would account for the generation of **28** and **29** upon protonolysis, and the reduction of alkenes during this process was evident from the formation of **27**, which can originate from either **21** or **22**.

Examination of the chain transfer-type rearrangement of **21a** to **22a** provided an increased understanding of this process. At a 0.10 M concentration of **18a**, acyclic hydrolysis products **27a** and **28a** were formed to the extent of 21 and 11%, respectively, and an increase in concentration to 0.25 M did not produce a significant increase in **28a**. Although the cyclization of **22a** has been observed with use of the stronger Lewis acid $EtAlCl_2$, compound **29** contributed only about 2% of the product mixture in each case. However, Grignard formation and transmetallation of **18a** at 0.44 M resulted in generation of comparable amounts of **28a** with an increase in the amount of **29a**. At 0.60 M, even greater amounts of **28a** and **29a** were produced. In contrast, generation of (β-D)-**21a**, prepared from 6-bromo-5-deuterio-1-hexene ((β-D)-**18a**), essentially shut down the formation of **28a** resulting from ligand transposition. Interestingly, formation of **27a** closely paralleled the possible generation of **25a** at this concentration. In each reaction, the diene resulting from β-hydrogen elimination of **21** was not observed. The concentration dependence of the ligand transposition process suggests that this transformation is an intermolecular reaction.

The reverse reaction, rearrangement of **22a** to **21a**, was demonstrated through independent generation of **22a** from **19a**, which resulted in 14% formation of the ligand transposition product **24a**. Studies with the six-membered ring analog **18b**, showed little effect of the tether length on the reaction, which further supported the intermolecular nature of this process. Substitution at the β-position with a phenyl substituent also produced comparable results in the formation of **27b**, **28b**, and **29b** through ligand transposition. In the case of **18c**, however, β-hydride elimination of the intermediate **20c** occurred to a greater extent, possibly due to greater steric interactions of the phenyl substituent with the ligands.

Free radical intermediates were not involved in the MgX_2 promoted ligand cyclization process. Under conditions used to generate free radical intermediates from **18a** (Bu_3SnH, AIBN, C_6H_6, 80°C, 0.05M), a 59:41 ratio of *trans*-**24a**/*cis*-**24a** resulted. In contrast, the *trans*-**24a**/*cis*-**24a** selectivity produced by the titanium/magnesium mediated cyclization of **18a** was > 97:3. Additional evidence against the formation of free radical intermediates was evident from the different *trans*-**24b**/*cis*-**24b** ratio produced by the MgX_2 promoted cyclization (44:56) when compared to that obtained for free radical cyclization of **18b** (59:41) [2]. In addition, while the MgX_2 promoted cyclization produced at least 61% conversion to **18b** under less favorable conditions for intramolecular bond formation (0.25 M), free radical cyclization conditions produced only 16% conversion of **18b** to **24b** at 0.05 M.

These model systems demonstrated the properties of β-hydrogen chain transfer proposed for the related Ziegler–Natta polymerization systems. The insertion and termination steps proceed through reaction with the titanium metal center, and these processes are highly dependent upon the reaction conditions, including solvent and Lewis acid cocatalyst. Based on the concentration dependence, and the absence of a chain length effect, the reaction appears to proceed in an intermolecular fashion for these model systems.

3. Experimental details

3.1. General methods

All reactions were conducted under nitrogen or argon atmospheres. THF, Et_2O, toluene, and benzene were distilled from sodium/benzophenone prior to use. Hexane was stirred over sulfuric acid, and after 5 d, the hexane was washed sequentially with H_2O, saturated aqueous $NaHCO_3$, dried ($CaCl_2$), and distilled from sodium/benzophenone/tetraglyme. The bromides used in these studies were prepared as previously reported [1,2,14]. Product distributions were determined by capillary gas chromatographic analysis of the quenched reaction mixture (HCl/Et_2O) using internal standards and correcting for detector response and were reproducible within ±2%.

NMR spectra were obtained on a Varian Gemini 300 or a VXR-300 instrument with $CDCl_3$ as solvent.

Signals are reported in units of ppm relative to $C(^1H)Cl_3$ or $^{13}CHCl_3$. Analytical gas chromatography (GC) was performed with a 50 m RSL200 column (5% methyl phenyl silicone equivalent to SE-54 or DB-5).

3.2. Activation of magnesium

The Mg used for formation of the Grignard reagents was activated prior to use by washing with 10% HCl, H_2O, acetone, and finally with Et_2O. The turnings were then flame dried in vacuo, and stored in a desiccator. Immediately prior to use, the reaction vessel containing the Mg was heated under vacuum for 15 min, purged with argon, evacuated and purged again with argon.

3.3. Competitive cyclization of Ti–R versus Al–R

3.3.1. 7-Iodo-6-propyl-1-heptene (6a) [28]

A mixture of the bromide (2.02 g, 9.2 mmol) and KI (15.30 g, 92.2 mmol) was heated at 60°C for 21 h. The mixture was then diluted with Et_2O (30 ml), washed with water (3 × 20 ml), saturated aqueous NaCl (20 ml), the organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo. The crude iodide was purified by Kugelrohr distillation (oven temperature 65–80°C, 3 Torr) to give **6a** (1.92 g, 7.2 mmol) in 78% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, $J = 6.4$ Hz, 3 H), 1.11–1.50 (m, 9 H), 1.99–2.01 (m, 2 H), 3.25 (d, $J = 4.4$ Hz, 2 H), 4.94 (m, 1 H), 5.00 (m, 1 H), 5.78 (ddt, $J = 16.9$, 10.2, 6.7 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.2, 16.5, 19.7, 25.8, 33.8, 33.9, 36.6, 38.3, 114.6, 138.7.

3.3.2. 7-Iodo-6-butyl-1-heptene (6b) [28]

3-Butylhept-6-en-1-ol (3.0 g, 17.7 mmol) was combined with NEt_3 (7.54 g, 71.0 mmol) and Et_2O (200 ml) and cooled to 0°C. Methane sulfonyl chloride (6.1 g, 53.2 mmol) was added over 15 min, and the mixture was stirred at 0°C for 1 h, warmed to room temperature, and stirred for an additional 12 h. After dilution with Et_2O (250ml), the mesylate was sequentially washed with saturated aqueous NH_4Cl (200 ml), H_2O (300 ml), and saturated aqueous NaCl (200 ml), dried over $MgSO_4$, and concentrated. The crude yellow oil was dissolved in acetone (175 ml), and NaI (10.92 g, 72.8 mmol) was added. The mixture was stirred at reflux until complete conversion to **6b** was achieved (approx. 6 h). The solution was cooled to ambient temperature, diluted with Et_2O (150 ml), washed with H_2O (3 × 100 ml), saturated aqueous $Na_2S_2O_3$ (1 × 175 ml) and saturated aqueous NaCl (1 × 75 ml). The organic layer was dried ($MgSO_4$), solvent was removed, and the iodide was distilled in vacuo (oven temperature 78–88°C, 3 Torr) to give **6b** (3.66 g, 14.3 mmol) in 81% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, $J = 7.1$ Hz, 3 H), 1.05–1.45 (m, 11 H), 1.98–2.04 (m, 2 H), 3.25 (d, $J = 4.5$ Hz, 2 H), 4.92 (ddt, $J = 10.2$, 2.2, 1.2 Hz, 1 H), 4.99 (ddt, $J = 17.0$, 3.6, 1.6 Hz, 1 H), 5.80 (ddt, $J = 17.0$, 10.2, 6.7 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.1, 16.6, 22.8, 25.8, 28.7, 33.8, 33.9, 34.1, 38.5, 114.6, 138.7.

3.3.3. Organoaluminum dichloride complexes (10)

A solution of **6** (2 mmol) in hexane (12 ml) and Et_2O (8 ml) was cooled to −78°C, and ^{t}BuLi (1.7 M in pentane, 4.34 mmol) was added over 3–4 min. In a separate Schlenk flask, a solution of $AlCl_3$ (2 mmol) in Et_2O (2.0 ml) was cooled to −78°C. The alkyllithium mixture was transferred via cannula to the $AlCl_3$ solution through a fritted funnel, and the resulting solution was stirred at −78°C for 20 min, and at 25°C for 3 h. The solvent was then removed in vacuo to afford a light yellow oil (**10**) which was taken on without further purification.

3.3.4. Alkyltitanocene dichloride (11)

Activated Mg turnings (12 mmol) were suspended in Et_2O (2 ml), and **7** (2 mmol) was added over a 2 h period. The solution was heated at reflux for an additional 1 h. In a separate flask, a solution of Cp_2TiCl_2 (2.4 mmol) in CH_2Cl_2 (8 ml) was prepared and cooled to −45°C. The Grignard solution was cooled to room temperature and transferred via cannula to the Cp_2TiCl_2, stirred for 0.5 h, and then allowed to warm to 25°C for an additional 5 h. Hexane (5 ml) was added, and the solution was concentrated in vacuo to about 3 ml. Hexane (5 ml) was added again, and the solution was passed through a fritted funnel to remove MgX_2 and Cp_2TiCl_2, and these solids were washed with toluene (2 × 7 ml). The supernatant was concentrated in vacuo to about 3 ml total volume, and hexane (5 ml) was added and the mixture was cooled to 0°C. The mixture was filtered again, and washed with toluene (2 × 5 ml) and concentrated in vacuo to afford a red oil (**11**) which was taken up in toluene (5 ml) and used without further purification.

Compound **11** was a stable, isolable mixture of the Ti–Cl (major) and Ti–Br (minor) species resulting from halide exchange with ClMgBr. During the transmetallation process, a mixture of Cp_2TiXR and MgX_2 are formed, in which the Br and Cl exchange to generate the various halogen combinations. **11b:** ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, $J = 7$ Hz, 3 H), 1.00–1.50 (m, 11 H), 2.01 (bq, $J = 7$ Hz, 2 H), 4.95–5.08 (m, 2 H), 5.81 (ddt, $J = 17$, 10, 7 Hz, 1 H), 5.87 (s, 10 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.8, 20.3, 26.6, 30.7, 33.6, 34.7, 36.5, 38.0, 114.6, 115.6, 139.2.

3.3.5 Competitive cyclization of Ti–R versus Al–R

Separate solutions of **10** and **11** were cooled to −78°C, and **11** was transferred via cannula over a 10

min period to **10** to produce a dark brown reaction mixture. Dodecane was added as an internal standard, and the heterogeneous mixture was stirred at −78°C for 0.5 h, then warmed to ambient temperature. A small amount of the crude reaction mixture was transferred via cannula into approximately 0.3 ml of a 1 M solution of HCl in Et_2O at −78°C. This sample was then filtered through a small column of basic alumina prior to analysis by capillary gas chromatography.

3.4. Chain transfer / ligand transposition

Activated Mg turnings (4 mmol) were suspended in Et_2O (1.0 ml), and the bromide was added dropwise over a period of 2 h. The solution was stirred at reflux for 3 h, and then transferred via cannula to a solution of Cp_2TiCl_2 (2.4 mmol) in toluene (4 ml) at ambient temperature. Methylcyclohexane was added as an internal standard for **18a**, **18b**, and **19a**, and dicyclohexyl was used for **18c**. After 12 h, aliquots were taken as described in 3.3.5. and analyzed by capillary gas chromatography.

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