Supporting Information for

Trimerization of Ethylene to 1-Hexene with Ti Complexes Bearing Phenoxy-Imine Ligands with Pendant Donors Combined with MAO

Yasuhiko Suzuki, Shinsuke Kinoshita, Atsushi Shibahara, Seiichi Ishii, Kazumori Kawamura,*

Yoshihisa Inoue, and Terunori Fujita*

Research Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan

Contents **Page**

1. General.

All manipulations of air- and/or moisture-sensitive compounds were conducted under an atmosphere of dried nitrogen using standard Schlenk tube techniques or in a dried nitrogen glovebox. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL 270 spectrometer at 270 MHz (^{1}H NMR) or 67.9MHz (^{13}C NMR) in $CDCl_3$ at ambient temperature. Chemical shifts are reported in δ units relative to the residual protons of $CDCl_3$ for ^{1}H NMR and the carbons of $CDCl_3$ for ^{13}C NMR. Gas chromatography (GC) analyses were conducted on Shimadzu GC-14A equipped with a FID detector and a J&W Scientific DB-5 column. In the case of GC-MS analyses, Shimadzu GC-17A equipped with a J&W Scientific DB-5 column was used. FD-MS spectra were recorded on an SX-102A from Japan Electron Optics Laboratory Co. Ltd. Elemental analyses were performed on a Perkin-Elmer 2400II elemental analyzer. X-ray analyses were performed by PharmAxess, Inc., Japan.

2. Materials.

Dried solvents (*n*-hexane, *n*-pentane, toluene, THF, MeOH, and EtOH) used for ligand and complex syntheses were purchased from Kanto Chemical Co., Inc. and Wako Pure Chemical Industries, Ltd., and were used as received without further purification. 2-Hydroxy-5-methyl-3-(2-phenylpropan-2-yl) benzaldehyde and 2-hydroxy-5-methyl-3-(1-adamantyl)benzaldehyde were prepared according to the literature procedure.[1] $TiCl_4(THF)_2$ and $TiCl_4$ as a 1.0 M toluene solution were purchased from Aldrich Chemical Company, Inc. and used without further purification. Cyclohexane used as an ethylene conversion reaction solvent (Wako Pure Chemical Industries, Ltd.) was dried over molecular sieves 4A and degassed by bubbling with nitrogen gas. Polymerization grade ethylene was obtained from Sumitomo Seika Co. Methylaluminoxane (MAO) was purchased from Tosoh Finechem Co. as a 1.5 M solution in *n*-hexane (trade name: MMAO-3A). All other chemicals were obtained from

commercial sources and used as received.

3. Ligand and Complex Syntheses.

Ligand Precursor Syntheses.

2-(2'-phenoxyphenyl)aniline (4). A suspension of 2-Phenoxyphenylboronic acid (7.70 g, 36.0 mmol), 2-bromoaniline (5.10 g, 30.0 mmol), palladium acetate (0.016 g, 0.075 mmol), and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.062 g, 0.150 mmol) in toluene (60 mL) was heated at 100 °C for 1 h. After the reaction, the resulting mixture was combined with water (100 mL) and was extracted with toluene. The extract was dried over $MgSO_4$, and then evaporated *in vacuo* to give a dark brown oil (7.5 g). The resulting dark brown oil was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (5/1) as eluent to afford **4** as a white solid in 77 % yield (5.99 g, 22.9 mmol). ^{1}H NMR (270MHz, $CDCl_3$): δ 7.40-6.97 (m, 9H, Ar-H), 6.90-6.87 (m, 2H, Ar-H), 6.77-6.69 (m, 2H, Ar-H), 3.65 (bs, 2H, NH_2).

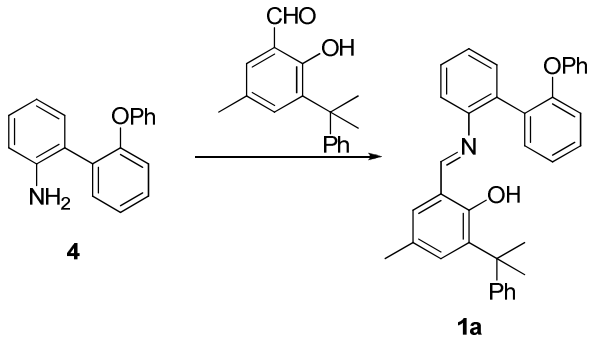
2-(2'-methoxyphenyl)aniline (5). A suspension of 2-methoxyphenylboronic acid (3.44 g, 20.0 mmol), 2-bromoaniline (3.44 g, 21.0 mmol), palladium chloride (0.355 g, 2.00 mmol), and triphenylphosphine (1.05 g, 4.00 mmol) in toluene (50 mL) was heated at 100 °C for 9.5 h. The reaction mixture was combined with water (50 mL) and was extracted with toluene. The extract was dried over $MgSO_4$, and then evaporated *in vacuo* to give a dark brown oil (6.3 g). The resulting dark brown oil was loaded on a silica gel column, and was eluted with *n*-hexane/ethyl acetate (3/1) to afford **5** as a white solid in 40 % yield (1.76 g, 8.83 mmol). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.38-6.98 (m, 6H, Ar-H), 6.85-6.75 (m, 2H, Ar-H), 3.80 (s, 6H, OCH_3), 3.67 (br, 2H, NH_2).

Ligand and Complex Syntheses.

***N*-(3-(2-phenylpropan-2-yl)-5-methylsalicylidene)-2'-(2"-phenoxyphenyl)aniline (1a)**. To a solution of **4** (1.37 g, 5.25 mmol) and 2-hydroxy-5-methyl-3-(2-phenylpropan- 2-yl)benzaldehyde

(1.27 g, 5.00 mmol) in EtOH (25 mL) was added one droplet of acetic acid. The mixture was stirred for 15 h at ambient temperature to afford a yellow suspension. The suspension was concentrated under reduced pressure to ca. 10 ml. The precipitate was collected by filtration, washed with EtOH (10 mL), and dried *in vacuo* to give **1a** as an orange powder in 70 % yield (1.74 g, 3.50 mmol). ^{1}H NMR (270MHz, $CDCl_3$): δ 12.75 (s, 1H, OH), 8.30 (s, 1H, N=CH), 7.35-6.88 (m, 18H, Ar-H), 6.73 (d, J = 7.6 Hz, 1.6 Hz, 1H, Ar-H), 6.61 (d, J = 8.3 Hz, 1H, Ar-H) , 2.32 (s, 3H, Ar-CH_3), 1.68 (s, 6H, cumyl-CH_3).

Scheme S1. Synthesis of **1a**

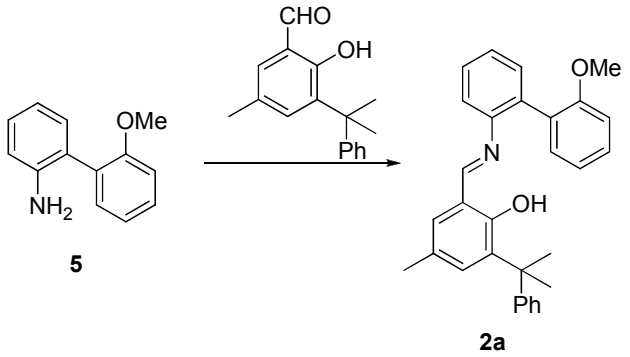


[*N*-(3-(2-phenylpropan-2-yl)-5-methylsalicylidene)-2'-(2"-phenoxyphenyl)anilinato] titanium(IV)trichloride (1). A solution of **1a** (0.498 g, 1.00 mmol) in THF (5.0 mL) was added dropwise to a solution of $TiCl_4(THF)_2$ (0.334 g, 1.00 mmol) in THF (10 mL) at -78 °C. The mixture was allowed to warm up to ambient temperature, and then stirred for 18 h to give a red solution. The solution was concentrated under reduced pressure to ca. 5 ml, and then *n*-hexane (20 mL) was added to give a red suspension. The precipitate was collected by filtration, washed with *n*-hexane (20 mL), and dried *in vacuo* to give **1** as an orange powder in 27 % yield (0.192 g, 0.266 mmol). ^{1}H NMR (270MHz, $CDCl_3$): 8.37 (s, 1H, N=CH), 7.50-7.44 (m, 2H, Ar-H), 7.30-6.97 (m, 15H, Ar-H), 6.94-6.71 (m, 3H, Ar-H), 3.46 (bs, 4H, THF), 2.30 (s, 3H, Ar-CH_3), 1.74 (bs, 6H, cumyl-CH_3), 1.55

(bs, 4H, THF). FD-MS: m/z = 651 (M^+, $C_{35}H_{30}Cl_3NO_2Ti$). Anal. Calcd for $C_{35}H_{30}Cl_3NO_2Ti \cdot C_4H_8O$: C, 64.79; H, 5.30; N, 1.94. Found: C, 64.50; H, 5.39; N, 1.71. Different from complexes **2** and **3**, the ^{1}H NMR spectrum of complex **1** exhibited only one broad singlet peak assigned to the methyl protons of a cumyl group, indicating ^{1}H NMR itself did not prove the facial coordination of the tridentate ligand in solution. There are several possibilities to understand the spectrum, e.g. overlapping of a pair of singlet peaks, different coordination mode from the facial and tridentate structure (meridional coordination or bidentate coordination), and rapid equilibrium between different structures in solution (facial/meridional, or bidentate/tridentade). Further studies concerning the structure of complex **1** are underway.

***N*-(5-methyl-3-(2-phenylpropan-2-yl)salicylidene)-2'-(2"-methoxyphenyl)aniline (2a).** To a solution of **5** (0.877 g, 4.40 mmol) and 2-hydroxy-5-methyl-3- (2-phenylpropan-2-yl)benzaldehyde (1.02 g, 4.01 mmol) in EtOH (20 mL) was added one droplet of acetic acid. The mixture was stirred for 18 h at ambient temperature, and then dried *in vacuo* to give an orange oil. Recrystallization from MeOH, then recrystallization from *n*-hexane gave **2a** as an orange-yellow solid in 74 % yield (1.29 g, 2.96 mmol). ^{1}H NMR (270MHz, $CDCl_3$): δ 12.92 (s, 1H, OH), 8.38 (s, 1H, N=CH), 7.38-7.07 (m, 12H, Ar-H), 6.98 (s, 1H, Ar-H), 6.89 (t, J = 7.4 Hz, 1H, Ar-H), 6.58 (d, J = 8.2 Hz, 1H, Ar-H), 3.31 (s, 3H, OCH_3), 2.32 (s, 3H, Ar-CH_3), 1.65 (s, 6H, cumyl-CH_3).

Scheme S2. Synthesis of **2a**

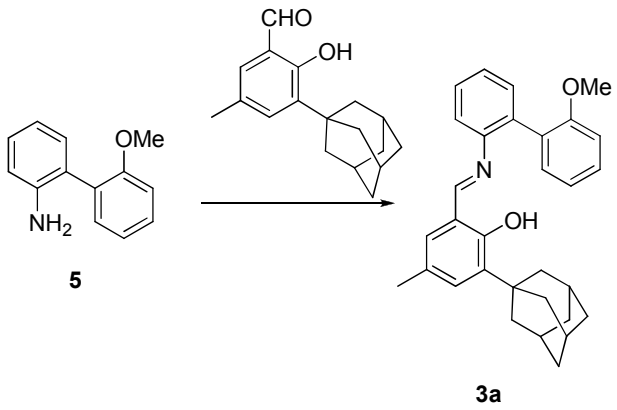


5 **2a**

[*N*-(5-methyl-3-(2-phenylpropan-2-yl)salicylidene)-2'-(2"-methoxyphenyl)anilinato] titanium(IV)trichloride (2). A solution of **2a** (0.218 g, 0.500 mmol) in toluene (10 mL) was dropwise added to a 1.0 M solution of $TiCl_4$ in toluene (0.55 mL, 0.550 mmol) over a period of 20 min at -78 °C. The mixture was allowed to warm up to ambient temperature and stirred for 12 h to afford an orange suspension. The precipitate was collected by filtration, washed with *n*-hexane (20 mL), and dried *in vacuo* to give **2** as an orange powder in 59 % yield (0.175 g, 0.297 mmol). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.90 (s, 1H, N=CH), 7.47-6.99 (m, 15H, Ar-H), 4.09 (s, 3H, OCH_3), 2.31 (s, 3H, Ar-CH_3), 1.85 (s, 3H, cumyl-CH_3), 1.67 (s, 3H, cumyl-CH_3). FD-MS: m/z = 537 (M^+ - CH_3Cl, $C_{29}H_{25}Cl_2NO_2Ti$). Anal. Calcd for $C_{30}H_{28}Cl_3NO_2Ti \cdot 0.5C_7H_8$: C, 63.38; H, 5.08; N, 2.21. Found: C, 63.34; H, 5.12; N, 1.91.

***N*-(5-methyl-3-(1-adamantyl)salicylidene)-2'-(2"-methoxyphenyl)aniline (3a). 3a** was prepared from **5** and 2-hydroxy-5-methyl-3-(1-adamantyl)benzaldehyde using a procedure similar to that for **2a**. Orange-yellow solid. The yield was 56 %. ^{1}H NMR (270 MHz, $CDCl_3$): δ 13.02 (s, 1H, OH), 8.48 (s, 1H, N=CH), 7.45-6.85 (m, 10H, Ar-H), 3.75 (s, 3H, OCH_3), 2.25 (s, 3H, Ar-CH_3), 2.11 (s, 6H, adamantyl-4,6,10-CH_2), 2.10 (s, 3H, adamantyl-CH), 1.78 (s, 6H, adamantyl-2,8,9-CH_2).

Scheme S3. Synthesis of **3a**



[*N*-(5-methyl-3-(1-adamantyl)salicylidene)-2'-(2"-methoxyphenyl)anilinato]titanium(IV) trichloride (3). 3 was prepared from **3a** and $TiCl_4$ using a procedure similar to that for **2**. Reddish-brown powder. The yield was 82 %. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.11 (s, 1H, N=CH), 7.58-7.04 (m, 10H, Ar-H), 4.44 (s, 3H, OCH_3), 2.34 (s, 3H, Ar-CH_3), 2.22 (bs, 6H, adamantyl-4,6,10-CH_2), 2.18 (bs, 3H, adamantyl-CH), 1.93 (d, J = 12 Hz, 3H, adamantyl-2,8,9-CH_2), 1.81 (d, J = 12 Hz, 3H, adamantyl-2,8,9-CH_2). FD-MS: m/z = 604 (M^+, $C_{31}H_{32}Cl_3NO_2Ti$). Anal. Calcd for $C_{31}H_{32}Cl_3NO_2Ti \cdot 0.5C_7H_8$: C, 63.66; H, 5.57; N, 2.15. Found: C, 63.61; H, 5.42; N, 2.19.

4. X-ray Structure Determination.

A single crystal of **3** ·0.5 diethyl ether suitable for an X-ray analysis was grown from diethyl ether/*n*-hexane. The ORTEP drawing shown in **Figure 2** in the text was drawn with 50% probability ellipsoids. The diethyl ether molecules were disordered.

5. Catalytic Ethylene Conversion.

Experimental Procedure (Table 1). A thoroughly nitrogen-purged 100-mL (500 mL for entries 4-6) autoclave was charged with cyclohexane (30 mL, (150 mL for entries 4-6)) and MAO (3.3 mL, 1.5 M *n*-hexane solution, 5.0 mmol). After the reactor was replaced with ethylene (0.1 MPa x 3), a 1.0 mL of Ti complex solution in toluene (0.50 mM, 0.50 μmol) was added. Then, ethylene pressure was elevated to a desired reaction pressure. The reaction was carried out for 60 minutes at 30 °C while maintaining the pressure by supplying ethylene. After the reaction, the remaining gas was evacuated from the reactor gradually, and then MeOH (1 ml) was added to the resulting solution to terminate the reaction. The evacuated gas was analyzed by GC (butenes and hexenes were not detected). The resulting reaction mixture was removed to separating funnel, washed with 0.1 N HCl aq. and then with water. Volatiles in the reaction mixture were separated from polyethylene by trap-to-trap vacuum transfer technique using a liquid nitrogen cold trap. The volatiles were analyzed by GC using an internal standard (*n*-nonane). Polyethylene was quantified by weight.

Ethylene Pressure Dependence of 1-Hexene Productivity. 1-Hexene productivity is plotted to ethylene pressure for ethylene conversion reaction with **3**/MAO in **Figure S1** (entries 3-6 in the **Table 1** in the text). The figure indicates a second order dependence of 1-hexene productivity on ethylene pressure.

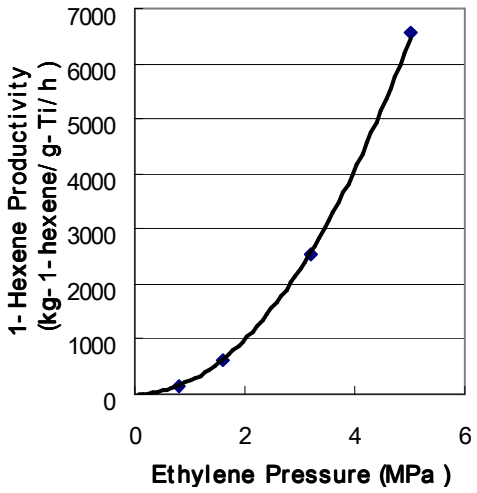


Figure S1. Plots of 1-hexene productivity vs ethylene pressure for the ethylene conversion reaction with **3**/MAO.

6. Decene By-Products

Characterizations. The by-products of this reaction, except for polyethylene, were observed on GC as a set of peaks around the C_{10} hydrocarbons regions (**Figure S2**). They were separated from the reaction mixture by filtration to remove polyethylene, and then by vacuum distillation to remove 1-hexene and solvents. The isolated by-products were identified with GC-MS, ^{1}H NMR and ^{13}C NMR. GC-MS fragmentation showed all of the compounds possessed decene structures (**Figure S3**). Furthermore, ^{1}H and ^{13}C NMR studies (**Figure S4 and S5**) indicated these compounds were a mixture of branched decenes, including 2-butyl-1-hexene as the predominant one. Selectivity of 2-butyl-1-hexene among decenes was ca. 90% determined by GC. ^{1}H and ^{13}C NMR spectra of 2-butyl-hexene generated from this ethylene conversion reaction were consistent with those reported previously.[2]

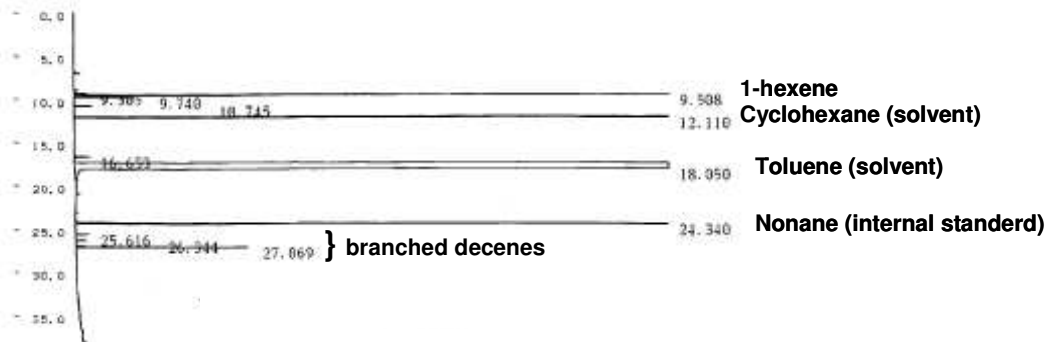


Figure S2. GC trace of reaction mixture.

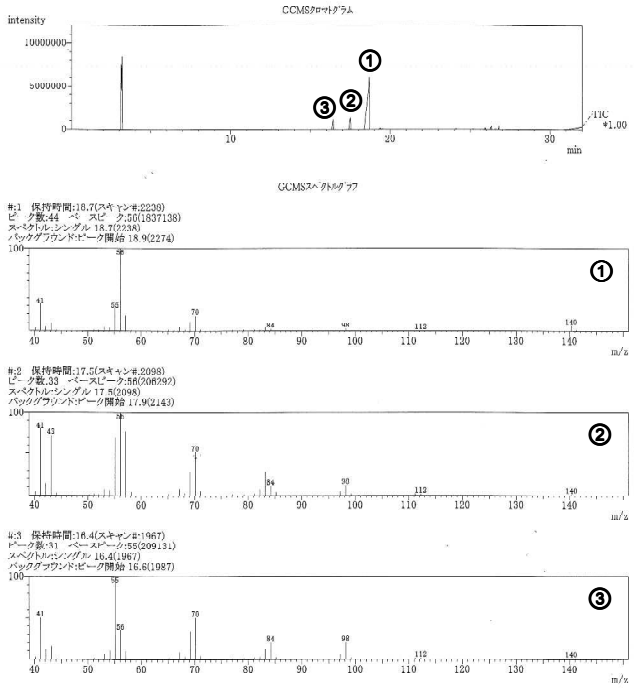


Figure S3. GC-MS spectrum of decenes isolated from the reaction mixture.

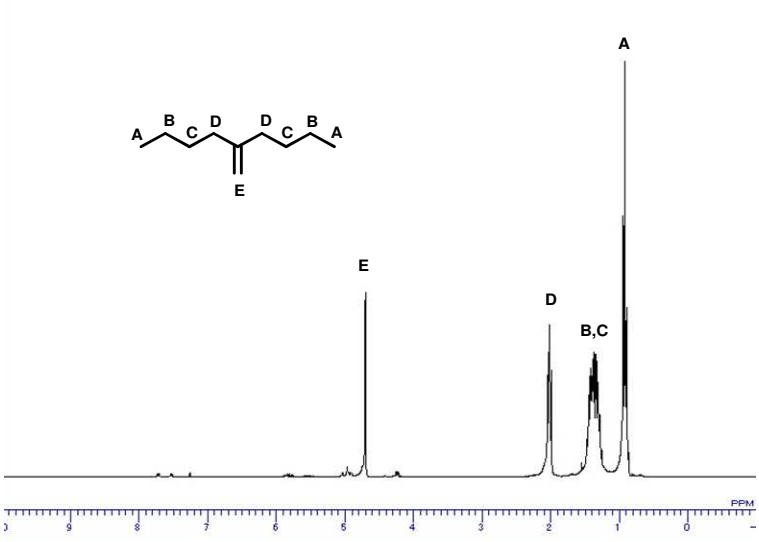


Figure S4. ^{1}H NMR spectrum of decenes isolated from the reaction mixture. Minor peaks arise from minor branched decene compounds.

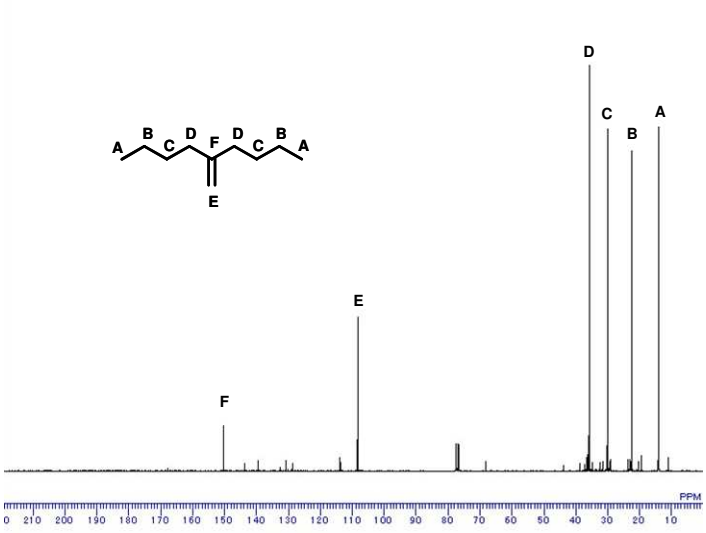


Figure S5. ^{13}C NMR spectrum of decenes isolated from the reaction mixture. Minor peaks arise derived from minor branched decene compounds.

Ethylene Pressure Dependence of 2-Butyl-1-hexene Productivity. 2-Butyl-1-hexene productivity is plotted to ethylene pressure for ethylene conversion reaction with **3**/MAO in **Figure S6.** 2-Butyl-1-hexene productivity also revealed a second order dependence on ethylene pressure.

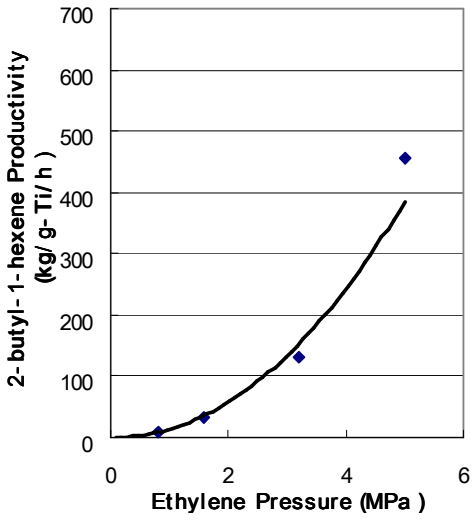
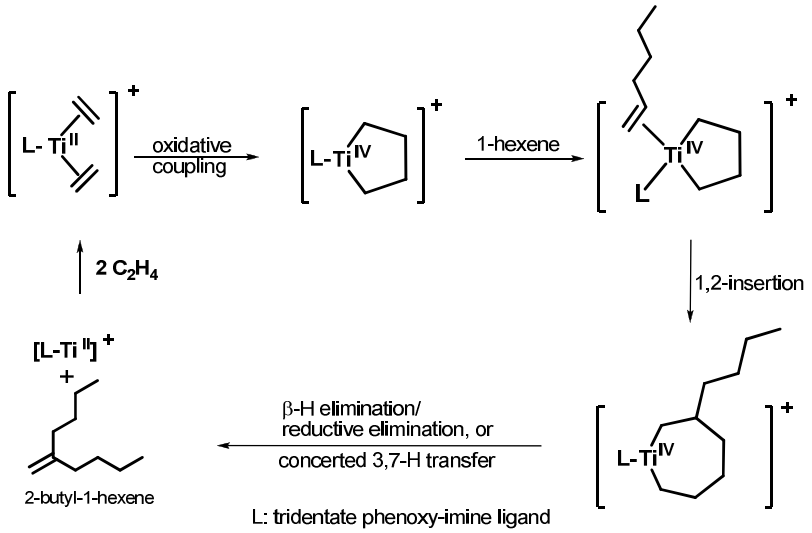


Figure S6. Plots of 2-butyl-1-hexene productivity vs ethylene pressure for the ethylene conversion reaction with **3**/MAO.

A Mechanism for the Formation of 2-Butyl-1-hexene. A plausible mechanism for the formation of 2-butyl-1-hexene is represented in **Scheme S4**. Considering that the formation of 2-butyl-1-hexene is second order in ethylene pressure **(Figure S6)**, 2-butyl-1-hexene is produced by a 1,2-insertion of 1-hexene into the metallacyclopentane to form a 3-butylmetallacycloheptane followed by β-H elimination/reductive elimination (or concerted 3,7-H transfer).

Scheme S4. A plausible mechanism for the formation of 2-butyl-1-hexene.



7. DFT calculations.

All calculations were performed at the gradient-corrected density functional BLYP level[3] by means of the Amsterdam Density Functional program (ADF2006.01).[4] For geometry optimizations, we used a triple ζ STO basis set on the titanium 3s, 3p, 3d, 4s, and 4p valence shells, and a double ζ STO basis set on the hydrogen (1s), and remaining first row atoms (2s, 2p). The inner shells without hydrogen atoms were treated within the frozen-core approximation. For energy calculations, the triple ζ STO basis set for the titanium, and titanium, and the double ζ plus polarization STO basis set for the other atoms were used, and the quasi-relativistic correction was

also added.

References:

(1) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847-6856.

(2) Kakiya, H.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2001**, *57*, 10063-10069.

(3) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) C. Lee, C.; W. Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett*. **1989**, *157*, 200.

(4) (a) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijder, J. G.; Ziegler, T. *J. Comput. Chem*. **2001**, *22*, 931 . (b) Fonseca Guerra, C.; Snijder, J. G.; te Velde, G.; Baerends, E. J. *Teheoret. Chem. Acc*. **1988**, *99*, 391. (c) *ADF2006.01, SCM*, *Theoretical Chemistry*, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.