SUPPORTING INFORMATION

Highly Selective Olefin Trimerization Catalysis by a Borane-Activated Titanium Trimethyl Complex

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General Considerations

All manipulations were performed using glovebox, high-vacuum, and/or Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified. Solvents were purified and degassed by using standard procedures. NMR spectra were acquired at 25 °C and measured on Varian spectrometers at field strengths of 300 MHz, 400 MHz, 500 MHz and 600 MHz. $^1$H chemical shifts are reported in ppm relative to SiMe$_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C$_6$D$_5$H, δ 7.14 for C$_6$D$_5$HCl). $^{13}$C chemical shift are reported in ppm relative to SiMe$_4$ (δ = 0) and were referenced internally with respect to the solvent (δ 128.06 for C$_6$D$_6$, δ 134.19 for C$_6$D$_5$Cl). Coupling constants are given in Hz. $^{19}$F and $^{11}$B chemical shifts are reported in ppm relative to the absolute $^1$H chemical shift reference. NMR spectra for (Fl)TiMe$_3$ and [(Fl)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] are shown in Appendix I. X-band EPR spectra were acquired at room temperature on a Bruker EMX spectrometer. 1,4-Dioxane, o-C$_6$H$_4$F$_2$, PhCl, 1-pentene, 1-hexene, 1-heptene, and 1-decene were dried over molecular sieves (3 Å) for at least two days, then filtered through activated alumina and stored over molecular sieves (3 Å) prior to use. C$_6$D$_6$ and C$_6$D$_5$Cl were dried over molecular sieves (3 Å) for at least two days prior to use.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table S3. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on $F^2$ with SHELXTL (Version 6.12). For additional information, crystallographic information files in CIF format can be obtained via the Internet at http://pubs.acs.org.
Gas Chromatography Analysis

Gas chromatography (GC) was performed on an Agilent 6890N instrument using a DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm film) and a flame ionization detector. Response factors were previously calculated. 4 Gas chromatography/mass spectrometry (GC-MS) was performed on an Agilent 6890N instrument using a HP-5MS column (30 m length, 0.25 mm diameter, 0.50 μm film) and an Agilent 5973N mass-selective EI detector.

Synthesis of 2-adamantyl-p-cresol

The synthesis of 2-adamantyl-p-cresol was adapted from the literature procedure.5 To a 500 mL round bottom flask equipped with a magnetic stir bar was added p-cresol (16.9 g, 0.156 mol), CH2Cl2 (150 mL), and 1-adamantanol (25.0 g, 0.164 mol) in air at room temperature. The colorless solution was stirred and treated dropwise with conc. H2SO4 (9 mL) over a period of 20 minutes, and then stirred for an additional 30 minutes. After this period, ice water (150 mL) was added slowly, and the solution was neutralized with NaOH(aq) (2 M, ca. 160 mL), producing a white slurry. CH2Cl2 (200 mL) was added and the organic layer was separated and collected. The aqueous layer was extracted with CH2Cl2 (2 × 200 mL), the organic portions were combined and washed with brine (100 mL), and the volatiles were removed by rotary evaporation giving a sticky white solid. The solid was treated with MeOH (200 mL), warmed to a gentle reflux, and then allowed to cool and filtered. The precipitate was extracted with an additional portion of MeOH (200 mL), filtered, and combined with the first MeOH extraction. The volatiles were removed by rotary evaporation, and the residue dried in vacuo giving 2-adamantyl-p-cresol as a white solid powder (27.1 g, 72% yield).
**Synthesis of 3-adamantyl-2-hydroxy-5-methylbenzaldehyde**

The synthesis of 3-adamantyl-2-hydroxy-5-methylbenzaldehyde was adapted from the literature procedure. To a 500 mL round bottom flask equipped with a magnetic stir bar was added 2-adamantyl-\(p\)-cresol (5.00 g, 0.021 mol), hexamethylenetetraamine (5.80 g, 0.041 mol) and glacial acetic acid (100 mL) in air, and the flask was fitted with a reflux condenser. The stirred mixture was heated at 110 °C for 5 hours, becoming a yellow solution. After this period, the solution was allowed to cool to 90 °C, the reflux condenser was removed and the flask was fitted with an addition funnel. \(\text{H}_2\text{O}\) (150 mL) was added dropwise to the yellow solution over a period of 30 minutes while the mixture cooled to room temperature, forming an off-white suspension (large solid dark yellow chunks occasionally formed; they were removed from the mixture and discarded). The precipitate was isolated by filtration, and was treated with MeOH (50 mL) and stirred for 1 hour. The mixture was then filtered, and the off-white precipitate was washed with MeOH (50 mL) and then dried in vacuo, giving 3-adamantyl-2-hydroxy-5-methylbenzaldehyde as an off-white solid (2.90 g, 52% yield).

**Synthesis of 2-(2'-methoxyphenyl)aniline**

The synthesis of 2-(2'-methoxyphenyl)aniline was adapted from the literature procedure. To a 350 mL ampoule equipped with a magnetic stir bar was added 2-methoxyphenylboronic acid (10.00 g, 0.066 mol), 2-bromoaniline (11.92 g, 0.069 mol), \(\text{Pd}(\text{PPh}_3)_4\) (1.91 g, 1.65 mmol), \(\text{K}_2\text{CO}_3\) (20.00 g, 0.145 mol) and toluene (200 mL). The ampoule was sealed, and the stirred mixture was heated at 115 °C for 16 hours. After this period, the mixture was allowed to cool to room temperature and \(\text{H}_2\text{O}\) (100 mL) was added. The organic layer was separated, and the aqueous layer was extracted with toluene (50 mL). The organic layers were combined, dried with \(\text{Na}_2\text{SO}_4\), filtered, and the volatiles removed by rotary evaporation, giving a dark brown oil. The oil was purified by flash column chromatography (silica gel, hexanes → hexanes/EtOAc 3:1
gradient) to give 2-(2′-methoxyphenyl)aniline as a white crystalline solid (5.20 g, 40% yield).

**Synthesis of (FI)H**

The synthesis of (FI)H was adapted from the literature procedure. To a 250 mL round bottom flask equipped with a magnetic stir bar was added 2-(2′-methoxyphenyl)aniline (4.26 g, 0.021 mol), 3-adamantyl-2-hydroxy-5-methylbenzaldehyde (5.50 g, 0.020 mol), EtOH (100 mL), and AcOH (ca. 0.2 mL) consecutively in air. The off-white suspension was stirred for 3 days at room temperature, thereby forming a bright yellow suspension. The yellow solid was isolated by filtration, washed with pentane (40 mL), and dried in vacuo, giving (FI)H as a yellow solid (6.00 g, 65% yield).

**Synthesis of (FI)TiCl₃**

The synthesis of (FI)TiCl₃ was adapted from the literature procedure. A solution of (FI)H (2.50 g, 5.54 mmol) in toluene (20 mL) was added dropwise to a solution of TiCl₄ in toluene (1M, 6.10 mL, 6.10 mmol) cooled to −78 °C. The mixture was allowed to warm to room temperature and stirred for ca. 16 hours, after which period the volatiles were removed in vacuo. The resulting dark red solid obtained was washed with toluene (1 × 20 mL, 1 × 10 mL), Et₂O (1 × 50 mL), and pentane (1 × 50 mL, 1 × 20 mL) and dried in vacuo giving (FI)TiCl₃ as a red solid powder (2.87 g, 86% yield).

**Synthesis of (FI)TiMe₃**

A solution of MeMgBr in Et₂O (1.41 mL, 3M, 4.23 mmol) was added to a stirring suspension of (FI)TiCl₃ (750 mg, 1.24 mmol) in Et₂O (10 mL) cooled to −35 °C, and stirred at −35 °C for 2 hours. After this period, 1,4-dioxane (0.75 mL, 8.8 mmol) was added, causing a precipitate to form, and the mixture was cooled at −35 °C for an additional 10 minutes. The suspension was then filtered through a medium porosity
frit with a 1 cm bed of celite, washed with cold Et₂O (−35 °C, 10 mL), and the wash discarded. The precipitate/celite was then extracted with cold Et₂O (−35 °C, 30 mL) and then room temperature Et₂O (2 × 30 mL). Each extract was filtered, concentrated to ca. 10 mL, layered with pentane (5 mL), and stored at −35 °C. It is important to note that the extracts should not be combined; yellow solutions occasionally darkened and deposited a black precipitate (see below). If this is observed, the solution should be filtered again at −35 °C, and stored at −35 °C to promote crystallization. The three extracts deposited yellow crystals after several days, which were isolated, washed with Et₂O (1 mL) and pentane (2 mL) and dried in vacuo to give (Fl)TiMe₃ as a yellow crystalline solid (172 mg, 26% yield). X-ray quality crystals were obtained by layering pentane onto a solution of (Fl)TiMe₃ in Et₂O at −35 °C; the molecular structure is shown in Figure S1.

Anal. calcd.: C, 75.1%; H, 7.6%; N, 2.6%. Found: C, 74.9%; H, 7.4%; N, 2.6%.

¹H NMR (CD₆₂): 1.72 [s, 9H of TiMe₃], 1.79 [d, AB pattern, ³J_H-H = 12, 3H of C(CH₃)₃(CH)₃(CH₂)₃], 1.92 [d, AB pattern, ³J_H-H = 12, 3H of C(CH₃)₃(CH)₃(CH₂)₃], 2.13 [br s, 3H of C(CH₃)₃(CH)₃(CH₂)₃], 2.19 [s, 3H of ArMe], 2.38 [br s, 6H of C(CH₃)₃(CH)₃(CH₂)₃], 2.93 [s, 3H of OMe], 6.25 [d, ³J_H-H = 8, 1H of Ar], 6.69 [s, 1H of Ar], 6.75 [t, ³J_H-H = 7, 1H of Ar], 6.89 [m, 2H of Ar], 7.07 [dt, ⁴J_H-H = 1, ³J_H-H = 8, 1H of Ar], 7.18 [m, 3H of Ar], 7.28 [d, ⁴J_H-H = 2, 1H of Ar], 8.31 [s, 1H of N=CH]. ¹³C¹H NMR (CD₆₂): 20.9 [s, 1C of ArMe], 29.6 [s, 3C of C(CH₃)₃(CH)₃(CH₂)₃], 37.5 [s, 3C of C(CH₃)₃(CH)₃(CH₂)₃], 40.9 [s, 3C of C(CH₃)₃(CH)₃(CH₂)₃], 54.7 [s, 1C of OMe], 70.1 [s, 3C of TiMe₃], 110.8 [s, 1CH of Ar], 121.5 [s, 1CH of Ar], 123.6 [s, 1C of Ar], 123.7 [s, 1CH of Ar], 126.5 [s, 1CH of Ar], 128.1 [s, 1C of Ar, located using 2D HMBC], 128.3 [s, 1C of Ar, located using 2D HMBC], 128.5 [s, 1CH of Ar], 129.8 [s, 1CH of Ar], 131.8 [s, 1CH of Ar], 132.6 [s, 1CH of Ar], 132.8 [s, 1CH of Ar], 132.9 [s, 1C of Ar], 134.6 [s, 1CH of Ar], 139.3 [s, 1C of Ar], 154.5 [s, 1C of Ar], 156.2 [s, 1C of Ar], 161.8 [s, 1C of Ar], 170.7 [s, 1C of N=CH].
Isolation of (FI)$_2$Mg and [(FI)MgBr]$_2$

When the reaction to synthesize (FI)TiMe$_3$ was conducted without the addition of 1,4-dioxane, it was observed that yellow solutions of (FI)TiMe$_3$ decomposed quickly and turned black at temperatures above 0 °C. Two byproducts of this decomposition were identified by X-ray crystallography as (FI)$_2$Mg and [(FI)MgBr]$_2$, and their molecular structures are shown in Figures S2 and S3, respectively.
**Figure S3.** Molecular Structure of [(Fl)MgBr]₂ (H atoms not shown for clarity).

**Reaction between (Fl)TiMe₃ and B(C₆F₅)₃**

A light yellow solution of (Fl)TiMe₃ (5 mg, 0.009 mmol) in either C₆D₅Cl (ca. 0.6 mL) or a mixture of C₆D₆ (ca. 0.6 mL) and o-C₆H₄F₂ (ca. 0.1 mL) in an NMR tube equipped with a J. Young valve was treated with B(C₆F₅)₃ (5 mg, 0.01 mmol) at room temperature, resulting in an immediate color change to yellow/orange. The sample was analyzed by ¹H, ¹³C, and ¹⁹F NMR spectroscopy, thereby demonstrating conversion to [(Fl)TiMe₂][MeB(C₆F₅)₃] (ca. 80% by ¹H NMR integration).

¹H NMR (C₆D₅Cl): 1.11 [br s, 3H of MeB(C₆F₅)₃], 1.73 [s, 3H of TiMe₂], 1.85 [s, 6H of C(CH₂)₃(CH)ₓ(CH₂)ₓ], 2.15 [s, 3H of ArMe], 2.15 [s, 3H of C(CH₂)₃(CH)ₓ(CH₂)ₓ], 2.28 [s, 6H of C(CH₂)₃(CH)ₓ(CH₂)ₓ], 4.20 [s, 3H of OMe], 6.41 [d, J_H-H = 8, 1H of Ar], 6.60 [s, 1H of Ar], 7.14 [m, 2H of Ar, under solvent signal], 7.24 [m, 4H of Ar], 7.39 [m, 2H of Ar], 7.86 [s, 1H of N=CH]. ¹³C{¹H} NMR (C₆D₅Cl): 11.2 [very br, 1C of MeB(C₆F₅)₃], 20.5 [s, 1C of ArMe], 29.2 [s, 3C of C(CH₂)₃(CH)ₓ(CH₂)ₓ], 37.0 [s, 3C of C(CH₂)₃(CH)ₓ(CH₂)ₓ], 37.6 [s, 1C of C(CH₂)₃(CH)ₓ(CH₂)ₓ], 41.3 [s, 3C of C(CH₂)₃(CH)ₓ(CH₂)ₓ], 70.9 [s, 1C of OMe], 81.5 [s, 1C of TiMe₂], 85.5 [s, 1C of TiMe₂],...
121.9 [s, 1CH of Ar], 124.8 [s, 1CH of Ar], 126.4 [s, 1C of Ar, located using 2D HMBC], 129.5 [s, 1C of Ar, located using 2D HMBC], 130.5 [s, 1CH of Ar], 130.5 [s, 1CH of Ar], 130.9 [s, 1CH of Ar], 131.0 [s, 1CH of Ar], 131.5 [s, 1CH of Ar], 131.5 [s, 1CH of Ar], 131.8 [s, 1C of Ar], 134.0 [s, 1C of Ar], 134.5 [s, 1CH of Ar], 136.9 [dm, 1J_{C-F} = 247, 6C of MeB(C₆F₅)], 137.8 [dm, 1J_{C-F} = 250, 3C of MeB(C₆F₅)], 138.2 [s, 1C of Ar], 138.9 [s, 1CH of Ar], 147.9 [s, 1C of Ar], 149.0 [dm, 1J_{C-F} = 236, 6C of MeB(C₆F₅)], 149.4 [s, 1C of Ar], 159.5 [s, 1C of Ar], 174.1 [s, 1C of N=CH], 3C of MeB(C₆F₅) not observed. ¹⁹F NMR (C₆D₅Cl): −166.7 [t, 3J_{F-F} = 19, 6F of MeB(C₆F₅), para-F], −164.3 [t, 3J_{F-F} = 21, 3F of MeB(C₆F₅), meta-F], −131.8 [d, 3J_{F-F} = 19, 6F of MeB(C₆F₅), ortho-F]. ¹¹B NMR (C₆D₅Cl): −14.4 [br s, 1 B of MeB(C₆F₅)].

¹H NMR (C₆D₅/0-C₆H₄F₂): 1.19 [br s, 3H of MeB(C₆F₅)], 1.56 [s, 3H of TiMe₂], 1.72 [s, 3H of TiMe₂], 1.85 [br s, 6H of C(CH₂)₃(CH₃)(CH₂)₃], 2.10 [s, 3H of ArMe], 2.15 [s, 3H of C(CH₂)₃(CH₃)(CH₂)₃], 2.27 [s, 6H of C(CH₂)₃(CH₃)(CH₂)₃], 3.69 [s, 3H of OMe], 5.98 [d, 3J_{H-H} = 8, 1H of Ar], 6.81 [m, 3H of Ar], 7.03 [m, 3H of Ar], 7.11 [dd, 3J_{H-H} = 8, 4J_{H-H} = 2, 1H of Ar], 7.22 [t, 3J_{H-H} = 8, 1H of Ar], 7.29 [d, 4J_{H-H} = 2, 1H of Ar], 7.57 [s, 1H of N=CH].

¹⁷F NMR (C₆D₅/0-C₆H₄F₂): −166.9 [t, 3J_{F-F} = 21, 6F of MeB(C₆F₅), para-F], −164.4 [t, 3J_{F-F} = 21, 3F of MeB(C₆F₅), meta-F], −131.8 [d, 3J_{F-F} = 22, 6F of MeB(C₆F₅), ortho-F]. ¹¹B NMR (C₆D₅/0-C₆H₄F₂): −14.2 [br s, 1 B of MeB(C₆F₅)].

The signals for the three methyl groups of [(Fl)TiMe₂][MeB(C₆F₅)] were confirmed by treating (Fl)Ti(¹³CH₃)₃ with B(C₆F₅), thereby producing [(Fl)Ti(¹³CH₃)₂][(¹³CH₃)B(C₆F₅)].

Selected ¹H NMR (C₆D₅Cl): 1.11 [d, 1J_{C-H} = 118, 3H of (¹³CH₃)B(C₆F₅)], 1.72 [d, 1J_{C-H} = 126, 3H of Ti(¹³CH₃)₂], 1.84 [d, 1J_{C-H} = 126, 3H of Ti(¹³CH₃)₂]. Selected ¹³C{¹H} NMR (C₆D₅Cl): 11.2 [br, 1C of (¹³CH₃)B(C₆F₅)], 81.5 [s, 1C of Ti(¹³CH₃)₂], 85.5 [s, 1C of Ti(¹³CH₃)₂].

Selected ¹H NMR (C₆D₅/0-C₆H₄F₂): 1.21 [d, 1J_{C-H} = 117, 3H of (¹³CH₃)B(C₆F₅)], 1.57 [d, 1J_{C-H} = 126, 3H of Ti(¹³CH₃)₂], 1.73 [d, 1J_{C-H} = 126, 3H of Ti(¹³CH₃)₂]. Selected ¹³C{¹H} NMR (C₆D₅/0-C₆H₄F₂): 11.4 [br, 1C of (¹³CH₃)B(C₆F₅)], 81.1 [s, 1C of Ti(¹³CH₃)₂], 84.8 [s, 1C of Ti(¹³CH₃)₂].
Ethylene Trimerization Catalysis with (FI)TiMe₃/B(C₆F₅)₃

In a typical experiment, a solution of (FI)TiMe₃ (3 – 5 mg, 0.006 – 0.009 mmol) in o-C₆H₄F₂ or PhCl (1 mL) in a 15 mL ampoule was treated with B(C₆F₅)₃ (3 – 5 mg, 0.006 – 0.01 mmol) at room temperature. The solution was frozen, degassed, and allowed to warm to room temperature. The ampoule was then charged with C₂H₄ (1 atm) and stirred for 1 – 3 hours under constant C₂H₄ pressure (1 atm) at room temperature. After this period, the volume of the solution had increased significantly (~0.3 – 1.0 mL), but only a trace amount of polymer (< 3 mg) had formed. Adamantane (10 – 20 mg, 0.07 – 0.15 mmol) was added as an internal integration standard, and the mixture was filtered through a plug of silica gel, diluted with benzene, and analyzed by GC. GC analysis demonstrated the catalytic production of 1-hexene, in addition to C₁₀ olefins and C₁₄ olefins, with a TOF of ca. 2.7×10³ mmol olefin oligomerized/mmol Ti/hr. The results of three experiments are shown in Table S1, and the corresponding gas chromatograms are shown in Figures S4–S6, respectively.

Table S1. Results of Ethylene trimerization catalysis with (FI)TiMe₃/B(C₆F₅)₃.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>(FI)TiMe₃/B(C₆F₅)₃ mg (mmol)</th>
<th>Solvent</th>
<th>Time h</th>
<th>1-Hexene mmol</th>
<th>C₁₀ Olefins mmol</th>
<th>C₁₄ Olefins mmol</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 (0.009)/5 (0.01)</td>
<td>o-C₆H₄F₂</td>
<td>1</td>
<td>2.36</td>
<td>2.47</td>
<td>0.30</td>
<td>2.7×10³</td>
</tr>
<tr>
<td>2</td>
<td>4 (0.007)/4 (0.008)</td>
<td>o-C₆H₄F₂</td>
<td>3</td>
<td>5.56</td>
<td>6.09</td>
<td>0.88</td>
<td>8.3×10³</td>
</tr>
<tr>
<td>3</td>
<td>3 (0.006)/3 (0.006)</td>
<td>PhCl</td>
<td>3</td>
<td>6.04</td>
<td>3.46</td>
<td>0.32</td>
<td>7.6×10³</td>
</tr>
</tbody>
</table>

Figure S4. GC of ethylene trimerization with (FI)TiMe₃/B(C₆F₅)₃ in o-C₆H₄F₂ for 1 hour (Expt. 1).
Three major C\textsubscript{10} olefins were produced in the ethylene trimerization catalysis with (Fl)TiMe\textsubscript{3}/B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, which can be seen in the gas chromatograms in Figures S4–S6. 1-Hexene was removed \textit{in vacuo}, and the C\textsubscript{10} olefins were identified by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy and GC analysis,\textsuperscript{8} and are shown in Figure S7. The \textsuperscript{1}H NMR spectrum is shown in Figure S8, with the olefinic peaks labeled with respect to Figure S7.
1H NMR Monitoring of Ethylene Trimerization Catalysis with (Fl)TiMe3/B(C6F5)3

A solution of (Fl)TiMe3 (3 mg, 0.006 mmol) in C6D6 (ca. 0.7 mL) and o-C6H4F2 (ca. 0.1 mL) in an NMR tube equipped with a J. Young valve was treated with B(C6F5)3 (3 mg, 0.006 mmol) at room temperature, thereby causing an immediate color change to yellow/orange. The sample was analyzed by 1H NMR spectroscopy, thereby demonstrating conversion to [(Fl)TiMe2][MeB(C6F5)3]. The solution was frozen, degassed, allowed to warm to room temperature, saturated with C2H4 (1 atm), shaken to promote mixing, and continually re-saturated with C2H4 until catalytic activity terminated. The sample was periodically analyzed by 1H NMR spectroscopy, demonstrating the catalytic production of 1-hexene with a slow disappearance of [(Fl)TiMe2][MeB(C6F5)3] (Figure S9). Approximate concentrations at each time point are listed in Table S2.
Figure S9. $^1$H NMR spectra of ethylene trimerization with [(FI)TiMe$_3$][MeB(C$_6$F$_5$)$_3$] ($t = 0$) in C$_6$D$_6$/o-C$_6$H$_4$F$_2$ (the height of the C$_6$D$_5$H signal (■) is constant in every spectrum; ■ = C$_6$D$_5$H, • = o-C$_6$H$_4$F$_2$, ◆ = C$_2$H$_4$, * = 1-hexene, ↓ = selected signals of [(FI)TiMe$_3$][MeB(C$_6$F$_5$)$_3$]).

Table S2. Approximate concentrations of [(FI)TiMe$_3$][MeB(C$_6$F$_5$)$_3$] and 1-hexene acquired from $^1$H NMR spectroscopic data.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[(FI)TiMe$_3$][MeB(C$_6$F$_5$)$_3$] (mM)</th>
<th>1-Hexene (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>3</td>
<td>33</td>
</tr>
<tr>
<td>60</td>
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</tr>
<tr>
<td>126</td>
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<td>161</td>
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<tr>
<td>194</td>
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<td>195</td>
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<tr>
<td>306</td>
<td>0</td>
<td>208</td>
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</table>

**EPR Monitoring of Ethylene Trimerization Catalysis with (FI)TiMe$_3$/B(C$_6$F$_5$)$_3$**

A solution of (FI)TiMe$_3$ (3 mg, 0.006 mmol) in C$_6$D$_6$ (ca. 0.7 mL) and o-C$_6$H$_4$F$_2$ (ca. 0.1 mL) in an NMR tube equipped with a J. Young valve was treated with B(C$_6$F$_5$)$_3$ (3 mg, 0.006 mmol) at room temperature, thereby causing an immediate color change to
yellow/orange, and $^1$H NMR spectroscopy confirmed conversion to [(Fl)TiMe$_2$][MeB(C$_6$F$_5$)$_3$]. The solution was then analyzed by EPR spectroscopy, indicating the formation of a Ti$^{\text{III}}$ species (Figure S10, blue trace), with an isotropic $g$ value of 1.958 at room temperature. The solution was frozen, degassed, allowed to warm to room temperature, saturated with C$_2$H$_4$ (1 atm), shaken to promote mixing, and was continually re-saturated with C$_2$H$_4$ until catalytic activity terminated. The sample was periodically analyzed by EPR and $^1$H NMR spectroscopy, revealing that (i) the intensity of the EPR signal for the Ti$^{\text{III}}$ species increased with time during catalysis, to $\sim$5× the initial value after 2 hours (Figure S10), and (ii) there was catalytic production of 1-hexene, with subsequent disappearance of the NMR signals for [(Fl)TiMe$_2$][MeB(C$_6$F$_5$)$_3$]. After catalysis terminated, the EPR signal for the Ti$^{\text{III}}$ was still intense (Figure S10, black trace).

**Figure S10.** EPR spectra of reaction of (Fl)TiMe$_3$ with B(C$_6$F$_5$)$_3$ in C$_6$D$_6$/o-C$_6$H$_4$F$_2$ (blue trace), and subsequent changes upon exposure to ethylene (double integration of EPR spectra shown in inset).

**Quantification of the Ti$^{\text{III}}$ Species**

A sample of Cp$_2$VCl$_2$ (1.2 mg, 0.005 mmol) in CH$_2$Cl$_2$ (0.8 mL, $\sim$6.0 mM) was prepared in an NMR tube equipped with a J. Young valve. A separate sample of (Fl)TiMe$_3$ (2.4 mg, 0.004 mmol) in C$_6$D$_6$ (ca. 0.7 mL) and o-C$_6$H$_4$F$_2$ (ca. 0.1 mL) was treated with B(C$_6$F$_5$)$_3$ (3 mg, 0.006 mmol) in an NMR tube equipped with a J. Young valve, having a total titanium concentration of $\sim$5.5 mM. Both samples were analyzed by EPR spectroscopy;
the doubly integrated spectrum of the titanium sample was ~20% of the intensity of vanadium sample, giving an approximate Ti\textsuperscript{III} concentration of 1.2 mM (corresponding to ~22% conversion to Ti\textsuperscript{III}). The titanium sample was also analyzed by \textsuperscript{1}H NMR spectroscopy, indicating that the missing intensity for the [(Fl)TiMe\textsubscript{2}]\textsuperscript{+} signals corresponds closely with the concentration of the Ti\textsuperscript{III} species. We can therefore estimate that the EPR signal of the Ti\textsuperscript{III} species tracks with the disappearance of the \textsuperscript{1}H NMR signals, and that the Ti\textsuperscript{III} species is the major Ti species present after 2 hours. Furthermore, three additional samples of Cp\textsubscript{2}VCl\textsubscript{2} were made with three different concentrations, and were also quantified by EPR spectroscopy, demonstrating that the intensity of the signal had a linear relationship with concentration. The EPR spectrum of one sample was also acquired at three different microwave powers, and the intensity of the signals were linear with the squared root of power, demonstrating that signal saturation was not a problem at the relevant concentrations. It is important to note that the inherent error in EPR spin quantification allows only for approximate determinations, as noted in the main text of the communication.

**C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}D\textsubscript{4} Trimerization Catalysis with (Fl)TiMe\textsubscript{3}/B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}**

A solution of (Fl)TiMe\textsubscript{3} (5 mg, 0.009 mmol) in PhCl (1 mL) in a 15 mL ampoule was treated with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (5 mg, 0.01 mmol) at room temperature. The solution was frozen, degassed, allowed to warm to room temperature, charged with a 1:1 mixture of C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}D\textsubscript{4} (1.5 atm) and stirred for 1 hour at room temperature. After this period, the mixture was filtered through a plug of silica gel, and analyzed by GC-MS. The 1-hexene fraction gave a 1:3:3:1 distribution in the mass spectrum with values (m/z) of 84, 88, 92, and 96, corresponding to the isotopologues C\textsubscript{6}H\textsubscript{12}, C\textsubscript{6}H\textsubscript{8}D\textsubscript{4}, C\textsubscript{6}H\textsubscript{4}D\textsubscript{8}, and C\textsubscript{6}D\textsubscript{12} (Figure S11).
Figure S11. Mass spectrum of 1-hexene fraction.

C₂D₄ Trimerization Catalysis with (Fl)TiMe₃/B(C₆F₅)₃

A solution of (Fl)TiMe₃ (5 mg, 0.009 mmol) in either C₆D₅Cl (ca. 0.6 mL) or a mixture of C₆D₆ (ca. 0.6 mL) and o-C₆H₄F₂ (ca. 0.1 mL) in an NMR tube equipped with a J. Young valve was treated with B(C₆F₅)₃ (5 mg, 0.01 mmol) at room temperature, resulting in the formation [(Fl)TiMe₂][MeB(C₆F₅)₃]. The solution was frozen, degassed, allowed to warm to room temperature, and then saturated with C₂D₄ (1 atm). The sample was analyzed by ¹H and ²H NMR spectroscopy, demonstrating the formation of CH₃D and the catalytic production of 1-hexene-₃D₁₂, respectively.

Ethylene/1-Heptene Trimerization Catalysis with (Fl)TiMe₃/B(C₆F₅)₃

A solution of (Fl)TiMe₃ (3 mg, 0.006 mmol) in o-C₆H₄F₂ (832 mg, 718 µL) in a 15 mL ampoule was treated consecutively with 1-heptene (196.4 mg, 282 µL, 2.0 mmol, 2M solution) and B(C₆F₅)₃ (3 mg, 0.006 mmol) at room temperature. The solution was frozen, degassed, and allowed to warm to room temperature. The stirring solution was then charged with C₂H₄ (1 atm) and stirred for 30 minutes under constant C₂H₄ pressure (1 atm) at room temperature. After this period, adamantane (10 mg, 0.07 mmol) was added as an internal integration standard, and the mixture was filtered through a plug
of silica gel, and analyzed by GC. GC analysis (Figure S12) demonstrated that the ratio of 1-hexene to C_{11} olefins produced is 3.43:1, and that ~7% of the 1-heptene was converted to C_{11} olefins during trimerization catalysis.

![Figure S12. Gas chromatogram of C_{2}H_{4}/1-heptene trimerization with (Fl)TiMe_{3}/B(C_{6}F_{5})_{3}.](image)

### 1-Pentene Trimerization Catalysis with (Fl)TiMe_{3}/B(C_{6}F_{5})_{3}

In a typical experiment, a mixture of (Fl)TiMe_{3} (1 mg – 5mg, 0.002 – 0.009 mmol) in 1-pentene (1 – 2 mL) was treated with B(C_{6}F_{5})_{3} (1 mg – 5mg, 0.002 – 0.01 mmol) at room temperature, thereby forming a suspension, which was stirred for 4 hours. After this period, adamantane (10 mg, 0.07 mmol) was added as an internal integration standard, and the solution was diluted with benzene, filtered through a plug of silica gel, and analyzed by GC. GC analysis (Figure S13) demonstrated the formation of C_{15} olefins with a TON of ca. 350 mmol 1-pentene oligomerized/mmol Ti, with no other detectible oligomers. The C_{15} region of the gas chromatogram displayed one major peak (~85%), with two other minor peaks (~15%).
1-Hexene Trimerization Catalysis with (FI)TiMe₃/B(C₆F₅)₃

In a typical experiment, a mixture of (FI)TiMe₃ (1 mg – 5mg, 0.002 – 0.009 mmol) in 1-hexene (1 – 2 mL) was treated with B(C₆F₅)₃ (1 mg – 5mg, 0.002 – 0.01 mmol) at room temperature, thereby forming a suspension, which was stirred for 4 hours. After this period, adamantane (10 mg, 0.07 mmol) was added as an internal integration standard, and the solution was diluted with benzene, filtered through a plug of silica gel, and analyzed by GC. GC analysis (Figure S14) demonstrated the formation of C₁₈ olefins with a TON of ca. 350 mmol 1-hexene oligomerized/mmol Ti, with no other detectible oligomers. The C₁₈ region of the gas chromatogram displayed one major peak (~85%), with two other minor peaks (~15%).
1-Decene Trimerization Catalysis with (FI)TiMe₃/B(C₆F₅)₃

In a typical experiment, a mixture of (FI)TiMe₃ (1 mg – 5mg, 0.002 – 0.009 mmol) in 1-decene (1 – 2 mL) was treated with B(C₆F₅)₃ (1 mg – 5mg, 0.002 – 0.01 mmol) at room temperature, thereby forming a suspension, which was stirred for 4 hours. After this period, adamantane (10 mg, 0.07 mmol) was added as an internal integration standard, and the solution was diluted with benzene, filtered through a plug of silica gel, and analyzed by GC. GC analysis (Figure S15) demonstrated the formation of C₃₀ olefins with a TON of ca. 100 mmol 1-decene oligomerized/mmol Ti, with no other detectible oligomers. The C₃₀ region of the gas chromatogram displayed one major peak (~85%), with two other minor peaks (~15%).

![Gas chromatogram of 1-decene trimerization with (FI)TiMe₃/B(C₆F₅)₃.](image)

**Figure S15.** Gas chromatogram of 1-decene trimerization with (FI)TiMe₃/B(C₆F₅)₃.

Analysis of Oligomers Formed in α-Olefin Trimerization Catalysis

GC analysis of the trimerization catalysis of α-olefins (1-pentene, 1-hexene and 1-decene) all give very similar chromatograms, with one major peak (85%) and two minor peaks (~15%), all of which correspond to trimers of the α-olefin. The major peak was determined to correspond to a set of diastereomers, which have been characterized by ¹H, ¹³C, DEPT 135°, HSQC, and HMBC NMR spectroscopies. Characterization and spectra for the C₁₅ olefin are described here, and the same analysis has been carried out for C₁₈ and C₃₀ olefins. There are eight possible olefins that can be produced in the
trimerization of α-olefins via the metallacycle mechanism (Figure S16); of these eight olefins, four are 2-substituted α-olefins (terminal olefins, H₂C=CRR’) and four are 1,2-substituted olefins (internal olefins, HRC=CHR’). The major regioisomer is assigned as a 2-substituted α-olefin based on the characteristic ¹H (δ = 4.86 ppm, Figure S17) and ¹³C (δ = 109.7 and 152.0 ppm, Figure S18) NMR chemical shifts and is confirmed by the phase-down vinylidene signal (CH₂) in the HSQC spectrum (Figure S19). Further analysis demonstrated the presence of two methine peaks (DEPT 135°, Figure S18, and HSQC, Figure S19), one of which is in an allylic position, which was confirmed by a three-bond (¹J_C-H) coupling of the vinylidene protons (CH₂) to the methine carbon (HMBC, Figure S20). Additionally, there are four methyl groups (¹³C NMR and DEPT 135°, Figure S18). There is only one regioisomer, shown in blue in Figure S16, with these features. ¹³C NMR spectroscopy indicated that the regioisomer is a pair of diastereomers, in an approximate 2:1 ratio.

**Figure S16.** Pathways to produce trimers of α-olefins via metallacycle mechanism (blue = major product).
Figure S17. $^1$H NMR spectrum of C$_{15}$ oligomers in C$_6$D$_6$.

Figure S18. $^{13}$C[$^1$H] NMR spectrum (bottom and middle) and $^{13}$C DEPT 135° spectrum (top) of C$_{15}$ oligomers in C$_6$D$_6$ ($\bullet$ = 1C of H$_2$C=CH, $\blacksquare$ = 1C of H$_2$C=C, $\bullet$ = 1C allylic methine, $\blacksquare$ = 1C methine). In the $^{13}$C DEPT 135° spectrum, methine (CH) and methyl (CH$_3$) peaks are phase up and methylene (CH$_2$) peaks are phase down.
**Figure S19.** 2D $^1$H-$^{13}$C HSQC NMR spectrum of C$_{15}$ oligomers in C$_6$D$_6$ (blue peaks are phase down (CH$_2$) and red peaks are phase up (CH and CH$_3$)).

**Figure S20.** 2D $^1$H-$^{13}$C HMBC NMR spectrum of C$_{15}$ oligomers in C$_6$D$_6$. 
### Table S3. Crystal, intensity collection and refinement data.

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Appendix I: NMR Spectra of (Fl)TiMe₃ and [(Fl)TiMe₂][MeB(C₆F₅)₃] at 25 °C.

^1H NMR of (Fl)TiMe₃ (C₆D₆)

^13C(^1H) NMR of (Fl)TiMe₃ (C₆D₆)
$^1$H NMR of [(Fl)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] (C$_6$D$_5$Cl)

$^{13}$C($^1$H) NMR of [(Fl)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] (C$_6$D$_5$Cl)

$^{19}$F NMR of [(Fl)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] (C$_6$D$_5$Cl)

$^{11}$B NMR of [(Fl)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] (C$_6$D$_5$Cl)
$^1$H NMR of \([(\text{F})\text{TiMe}_2][\text{MeB(C}_6\text{F}_5)_3]\) (C$_6$D$_6$/o-C$_6$H$_4$F$_2$)

$^{19}$F NMR of \([(\text{F})\text{TiMe}_2][\text{MeB(C}_6\text{F}_5)_3]\) (C$_6$D$_6$/o-C$_6$H$_4$F$_2$)

$^{11}$B NMR of \([(\text{F})\text{TiMe}_2][\text{MeB(C}_6\text{F}_5)_3]\) (C$_6$D$_6$/o-C$_6$H$_4$F$_2$)
References:

(b) Burger, B. J.; Bercaw, J. E. in Experimental Organometallic Chemistry; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.


(9) The concentration of a saturated C2H4 (1 atm) solution was determined to be ca. 100 mM by using 1H NMR spectroscopy with an internal integration standard,