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Lewis Acid Promoted Titanium Alkylidene Formation: Off-Cycle Intermediates Relevant to Olefin Trimerization Catalysis[‡]

Aaron Sattler, David G. VanderVelde, Jay A. Labinger,* and John E. Bercaw*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, United States

ABSTRACT: Two new precatalysts for ethylene and α -olefin trimerization, (FI)Ti(CH₂SiMe₃)₂Me and (FI)Ti(CH₂CMe₃)₂Me (FI = phenoxy-imine), have been synthesized and structurally characterized by X-ray diffraction. (FI)Ti(CH₂SiMe₃)₂Me can be activated with one equivalent of B(C₆F₅)₃ at room temperature to give the solvent-separated ion pair [(FI)Ti(CH₂SiMe₃)₂][MeB(C₆F₅)₃], which catalytically trimerizes ethylene or 1-pentene to produce 1-hexene or C₁₅ olefins, respectively. The neopentyl analogue, (FI)Ti(CH₂CMe₃)₂Me, is unstable towards activation with B(C₆F₅)₃ at room temperature, giving no discernible diamagnetic titanium complexes, but at -30 °C the following can be observed by NMR spectroscopy: (i) formation of the *bis*-neopentyl cation [(FI)Ti(CH₂CMe₃)₂]⁺, (ii) α -elimination of neopentane to give the neopentylidene complex [(FI)Ti(=CHCMe₃)]⁺, and (iii) subsequent conversion to the imido-olefin complex [(Me-OAr₂N=)Ti(OArHC=CHCMe₃)]⁺ via an intramolecular metathesis reaction with the imine fragment of the (FI) ligand. If the reaction is carried out at low temperature in the presence of ethylene, catalytic production of 1-hexene is observed, in addition to the titanacyclobutane complex [(FI)Ti(CH(CMe₃)CH₂CH₂)]⁺, resulting from addition of ethylene to the neopentylidene [(FI)Ti(=CHCMe₃)]⁺. None of the complexes observed spectroscopically subsequent to [(FI)Ti(CH₂CMe₃)₂]⁺ is an intermediate or precursor for ethylene trimerization, but notwithstanding these off-cycle pathways, [(FI)Ti(CH₂CMe₃)₂]⁺ is a precatalyst that undergoes rapid initiation to generate a catalyst for trimerizing ethylene or 1-pentene.

INTRODUCTION

The catalytic synthesis of 1-hexene by selective ethylene trimerization, an important industrial process¹ due to its use as a comonomer in the production of linear low-density polyethylene (LLDPE), has been extensively studied.² Although catalytic systems have been known for many years,³ there has been little advance in understanding what makes a catalyst trimerize rather than polymerize ethylene. The rational development of new catalysts necessitates information about the active catalytic species, which is often difficult to observe spectroscopically or characterize structurally. Often the major species that can be observed is not part of the catalytic cycle;⁴ furthermore, the large excess of aluminum reagents typically required for activation, such as methylaluminoxane (MAO), impedes mechanistic studies.

An interesting trimerization system, reported by Fujita and co-workers, is generated from (FI)TiCl₃ [(FI = (*N*-(5-methyl-3-(1-adamantyl)salicylidene)-2'--(2"-methoxyphenyl)anilinato)] and MAO (10,000 equivalents); it produces 1-hexene with a turnover number (TON) of $\sim 1.1 \times 10^7$ mmol olefin oligomerized/mmol Ti at 49.3 atm of ethylene.⁵ We recently reported that (FI)TiMe₃, a putative intermediate upon treatment of (FI)TiCl₃ with MAO,^{5,6} can be independently synthesized and activated with just one equivalent of B(C₆F₅)₃ to give [(FI)TiMe₂][MeB(C₆F₅)₃], an active precatalyst for ethylene trimerization.⁷ Furthermore, (FI)TiMe₃/B(C₆F₅)₃ was shown to selectively trimerize α -olefins,

and is the second system known to do so.⁸ Trimerization of α -olefins is important to produce value-added substances such as diesel and/or jet fuel, and motor lubricants.⁹ The ability to stoichiometrically produce a trimerization precatalyst, [(FI)TiMe₂][MeB(C₆F₅)₃], allowed us to show that: (i) the relative rate of initiation is orders of magnitude slower than trimerization; (ii) the decomposition rate is similar to that of initiation; and (iii) initiation proceeds by a series of steps involving ethylene insertion(s), β -H elimination and reductive elimination of methane. Under such conditions, only the precatalyst [(FI)TiMe₂][MeB(C₆F₅)₃], the decomposition product (a Ti^{III} species), and 1-hexene could be experimentally observed.

In order to ascertain information about the active catalytic species, we sought a system in which precatalyst initiation is *faster* than trimerization. Previous studies on the propylene polymerization catalysts [Cp*₂CpZrR][MeB(C₆F₅)₃] (R = Me, CH₂SiMe₃, CH₂CMe₃) have shown that insertion of propylene into the zirconium-alkyl bond (i.e., catalyst initiation) is significantly faster for Zr-CH₂CMe₃ compared with Zr-Me and Zr-CH₂SiMe₃; the [Cp*₂CpZr(CH₂CMe₃)][MeB(C₆F₅)₃] system thus allowed for a detailed kinetic analysis of propylene propagation, rather than being limited by slow initiation.¹⁰ It is important to note that, based on the proposed mechanisms for selective trimerization catalysis (Scheme 1),^{5,7,11} the active catalyst should be the same (i.e., [(FI)Ti^{III}(C₂H₄)₂]⁺), independent of the alkyl ligands in the precatalyst.

[‡] Dedicated in memory of Greg Hillhouse, a friend, colleague, and outstanding organometallic chemist.

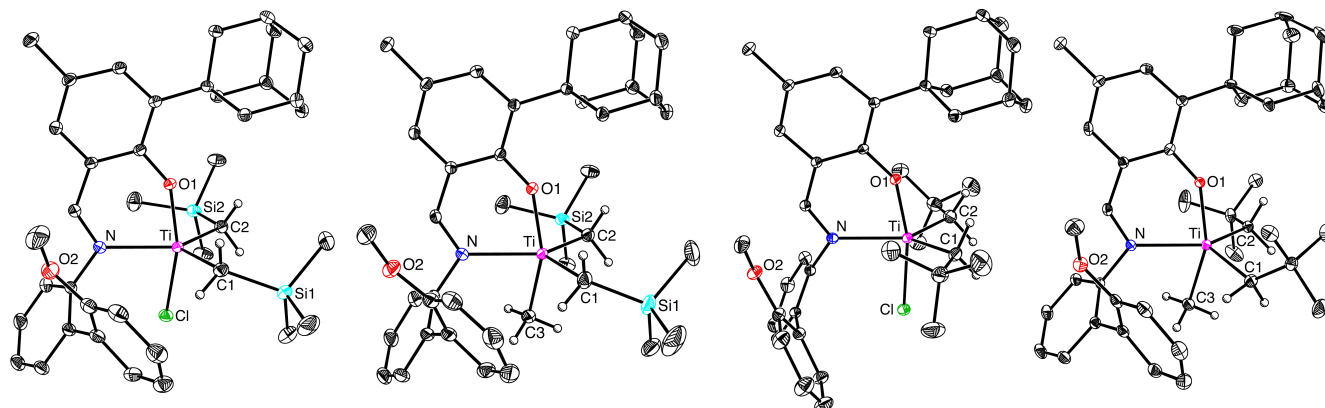
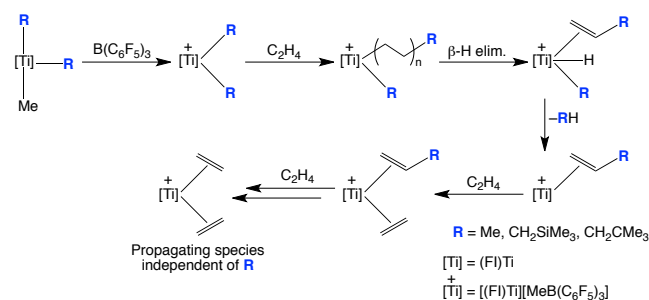


Figure 1. Molecular structures of (FI)Ti(CH₂SiMe₃)₂Cl, (FI)Ti(CH₂SiMe₃)₂Me, (FI)Ti(CH₂CMe₃)₂Cl and (FI)Ti(CH₂CMe₃)₂Me (left to right). The hydrogen atoms on the (FI) ligand, CH₂SiMe₃ methyls, and CH₂CMe₃ methyls are not shown for clarity.

Accordingly, we report here the synthesis of two new potential trimerization precatalysts, (FI)Ti(CH₂SiMe₃)₂Me and (FI)Ti(CH₂CMe₃)₂Me, and their behavior upon activation with one equivalent of B(C₆F₅)₃. While both systems are complicated by competing reactions involving the (FI) and alkyl ligands, each selectively catalyzes trimerization of ethylene and 1-pentene and the one based on (FI)Ti(CH₂CMe₃)₂Me does, indeed, undergo faster initiation.

Scheme 1.



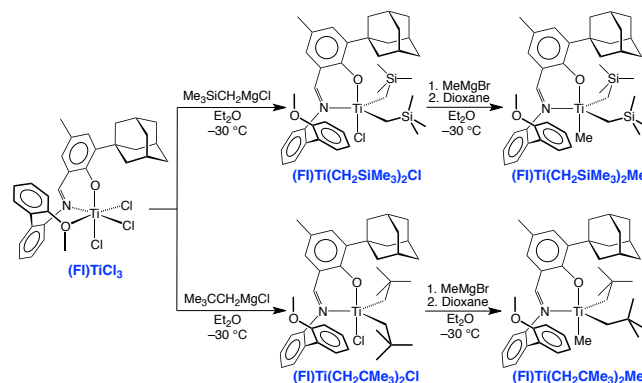
RESULTS AND DISCUSSION

1. Synthesis and Structural Characterization of (FI)Ti Complexes. (FI)Ti(CH₂SiMe₃)₂Me and (FI)Ti(CH₂CMe₃)₂Me were synthesized by consecutive treatment of a suspension of (FI)TiCl₃ in Et₂O with the appropriate Grignard reagents, Me₃SiCH₂MgCl or Me₃CCH₂MgCl (2.5 equiv), respectively, and MeMgBr (2.4 equiv) at –30 °C, followed by addition of 1,4-dioxane (Scheme 2).¹² The corresponding chlorides, (FI)Ti(CH₂SiMe₃)₂Cl and (FI)Ti(CH₂CMe₃)₂Cl, could be isolated and characterized when the reactions were carried out without MeMgBr addition. All four complexes are soluble in pentane, allowing for easier purification and higher isolated yields compared with (FI)TiMe₃, which is only sparingly soluble in pentane. Each complex has been structurally characterized by X-ray diffraction, and the molecular structures are shown in Figure 1; all are five-coordinate with the methoxy group not coordinated to the Ti center in the solid state, displaying approximate trigonal bipyramidal geometries distorted towards square pyramidal. The hydrogen atoms of the methylene groups (CH₂XMe₃; X = Si, C) were located in the difference electron density map and freely refined, and show no indication of any α -agostic interaction.¹³

One structural feature of note is that the largest of the three angles in the pseudo trigonal plane in (FI)Ti(CH₂SiMe₃)₂Cl, (FI)Ti(CH₂SiMe₃)₂Me and (FI)Ti(CH₂CMe₃)₂Me is distal to the

methoxy-arene group (C2–Ti–N), whereas the largest angle in (FI)TiMe₃ is proximal (N–Ti–C1),⁷ suggesting that the sterics of the XMe₃ (X = Si, C) groups have a more significant effect on distorting the geometry towards square pyramidal than does the arene. This is most readily seen by comparing the distal and proximal angles (Δ_{d-p}) in Table 1. Although (FI)Ti(CH₂CMe₃)₂Cl has the same approximate geometry about the Ti center as the other complexes above, the neopentyl ligands are related by a pseudo mirror plane (Figure 1) such that the distal and proximal angles are more similar (Table 1).

Scheme 2.



¹H and ¹³C NMR spectroscopic studies indicate that all of the complexes are five-coordinate in solution as well, based on the upfield chemical shift of the OMe signal relative to that of (FI)TiCl₃.⁵ The fluxional nature of the complexes depends on whether the fifth ligand is a chloride or methyl group: at 25 °C (FI)Ti(CH₂SiMe₃)₂Me and (FI)Ti(CH₂CMe₃)₂Me each display a single ¹H NMR signal for their respective (CH₂XMe₃)₂ (X = Si, C) methyl groups, while (FI)Ti(CH₂SiMe₃)₂Cl and (FI)Ti(CH₂CMe₃)₂Cl each display two signals. Furthermore, the chloride complexes display four chemically inequivalent signals for the methylene protons (CH₂XMe₃; X = Si, C) at 25 °C, one of which is significantly upfield of the other three (δ = 0.25 and 1.04 ppm, respectively). Although upfield chemical shifts can indicate α -agostic interactions,¹³ the absence of any such interaction in the solid-state structures lead us to believe that the diamagnetic ring current of the methoxy-arene is a more likely cause.

Table 1. Bond angles (°) of the pseudo trigonal plane of five coordinate (FI)Ti complexes.

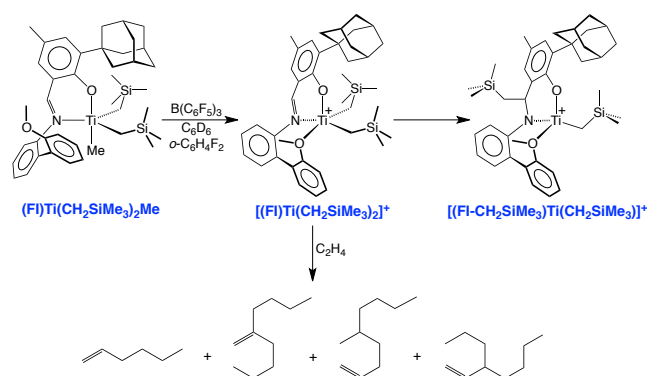
	N-Ti-C1 ^a	C1-Ti-C2	C2-Ti-N ^b	Δ_{d-p} ^c
(FI)Ti(CH ₂ SiMe ₃) ₂ Cl	115.71(5)	106.15(6)	137.96(5)	22.25
(FI)Ti(CH ₂ SiMe ₃) ₂ Me	116.30(5)	106.60(6)	137.10(5)	20.80
(FI)Ti(CH ₂ CMe ₃) ₂ Cl	132.74(4)	100.98(4)	126.13(4)	-6.61
(FI)Ti(CH ₂ CMe ₃) ₂ Me	115.63(9)	103.76(10)	140.17(8)	24.54
(FI)TiMe ₃ ^d	131.00(7)	107.83(8)	121.01(6)	-9.99

^a Angle proximal to the methoxy-arene. ^b Angle distal to the methoxy-arene. ^c $\Delta_{d-p} = (C2-Ti-N) - (N-Ti-C1)$. ^d The labeling for (FI)TiMe₃ is different; the angles (left to right) correspond to: N-Ti-C2, C2-Ti-C3, C3-Ti-N (reference 7).

2. Activation and Catalysis with (FI)Ti(CH₂SiMe₃)₂Me.

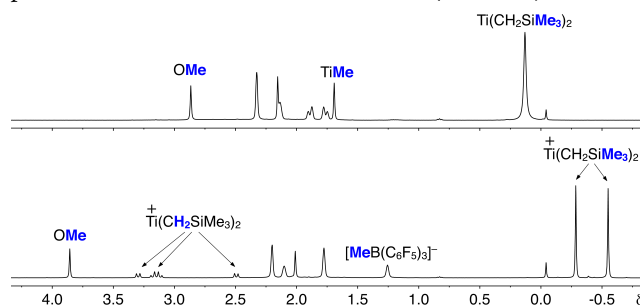
When a solution of (FI)Ti(CH₂SiMe₃)₂Me in C₆D₆/o-C₆H₄F₂ (ca. 0.65 mL/0.05 mL) is treated with one equivalent of B(C₆F₅)₃, selective methide abstraction gives the solvent-separated ion pair [(FI)Ti(CH₂SiMe₃)₂][MeB(C₆F₅)₃] (Scheme 3, [MeB(C₆F₅)₃]⁻ anion not shown in all Schemes). The ion pair has spectroscopic features very similar to [(FI)TiMe₂][MeB(C₆F₅)₃]:⁷ (i) a downfield OMe chemical shift compared with (FI)Ti(CH₂SiMe₃)₂Me, indicating coordination to the Ti center;¹⁴ (ii) a $\Delta\delta(m,p-F)$ of 2.5 ppm in the ¹⁹F NMR spectrum, suggesting a non-coordinating solvent-separated anion;¹⁵ and (iii) chemically inequivalent and static SiMe₃ groups in the ¹H NMR spectrum at 25 °C ($\delta = -0.50$ and -0.24 ppm, Figure 2). Furthermore, there are four distinct signals for the methylene protons (CH₂SiMe₃), in accord with a non-fluxional structure (Figure 2).

Scheme 3.

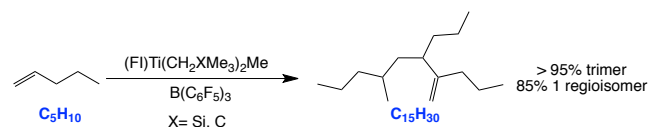


Upon treatment of the [(FI)Ti(CH₂SiMe₃)₂][MeB(C₆F₅)₃] solution with ethylene (1 atm), 1-hexene is produced rapidly, with slow disappearance of [(FI)Ti(CH₂SiMe₃)₂]⁺ as determined by ¹H NMR spectroscopy. Hence, as for [(FI)TiMe₂][MeB(C₆F₅)₃],⁷ the rate of trimerization is significantly greater than the rate of initiation. Under a constant pressure of ethylene (1 atm), a solution of (FI)Ti(CH₂SiMe₃)₂Me/B(C₆F₅)₃ (9 μmol, 9 mM) in o-C₆H₄F₂ (1 mL) at 25 °C produces primarily 1-hexene and C₁₀ olefins, with only trace amounts of polyethylene formed (< 3 mg). The activity (TON of ca. 4.1 × 10³ mmol olefin oligomerized/mmol Ti after ca. 3 h) is about half that obtained with [(FI)TiMe₂][MeB(C₆F₅)₃] (Table 2).

(FI)Ti(CH₂SiMe₃)₂Me/B(C₆F₅)₃ also trimerizes α-olefins such as 1-pentene, giving a TON of ca. 900 (Table 2), almost three times greater than (FI)TiMe₃/B(C₆F₅)₃.⁷ The higher TON is attributed to greater solubility of (FI)Ti(CH₂SiMe₃)₂Me in 1-pentene compared with (FI)TiMe₃ which forms a suspension with some solid immobilized on the walls of the flask. It is important to note that selectivity for trimers is greater than 95%, and that 85% of the trimers are the same regioisomer (Scheme 4) as observed for (FI)TiMe₃/B(C₆F₅)₃,⁷ strongly suggesting that (FI)Ti(CH₂SiMe₃)₂Me and (FI)TiMe₃ produce the same active catalyst. Likewise, the main decomposition product is the same for both precatalysts: a Ti^{III} species exhibiting a room temperature EPR signal with an isotropic *g* value of 1.958.⁷ When monitoring the ethylene trimerization by EPR spectroscopy, the signal intensity increases over the course of catalysis and reaches a maximum after catalysis has stopped. All of this is consistent with the proposed mechanism of trimerization initiation (Scheme 1).

**Figure 2.** ¹H NMR spectra of (FI)Ti(CH₂SiMe₃)₂Me in C₆D₆ (top) and [(FI)Ti(CH₂SiMe₃)₂][MeB(C₆F₅)₃] in C₆D₆/o-C₆H₄F₂ (bottom) at 25 °C (aromatic region not shown).

Scheme 4.

**Table 2.** Ethylene and 1-pentene trimerization catalysis at 25 °C.

	Ethylene ^a		1-Pentene ^b
	TON ^c	TOF ^d	TON ^e
(FI)TiMe ₃ ^e	8.3 × 10 ³	2.7 × 10 ³	3.5 × 10 ²
(FI)Ti(CH ₂ SiMe ₃) ₂ Me	4.1 × 10 ³	1.2 × 10 ³	9.0 × 10 ²
(FI)Ti(CH ₂ CMe ₃) ₂ Me ^f	2.5 × 10 ³	7.5 × 10 ³	5.0 × 10 ²

^a Reaction time is 3 hours for a typical run. ^b Reaction time is ca. 12 hours for a typical run. ^c TON = mmol olefin oligomerized/mmol Ti. ^d TOF = TON/h. ^e Taken from reference 7. ^f Reaction time is 20 minutes.

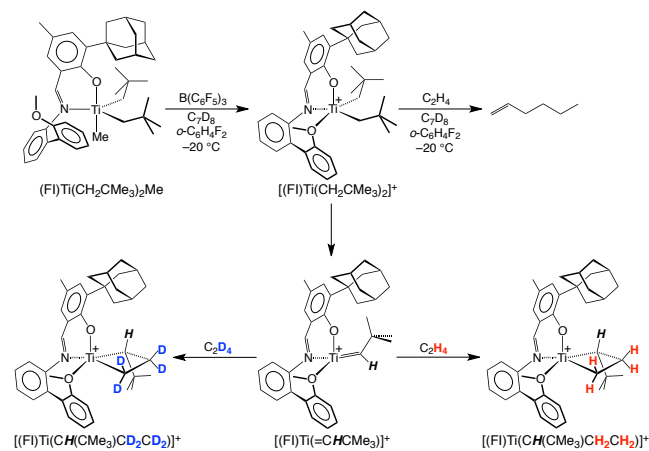
While monitoring catalysis with [(FI)Ti(CH₂SiMe₃)₂]⁺ in C₆D₆/o-C₆H₄F₂ (ca. 0.65 mL/0.05 mL) by ¹H NMR spectroscopy, we observed a new diamagnetic species, which we formulate as [(FI-CH₂SiMe₃)Ti(CH₂SiMe₃)]⁺, an isomer of the parent cation [(FI)Ti(CH₂SiMe₃)₂]⁺ resulting from the migration of one CH₂SiMe₃ group to the imine carbon of the (FI) ligand (Scheme 3).¹⁶ Key new ¹H NMR spectroscopic features include (i) a methine signal at $\delta = 4.15$ ppm ($\delta(^{13}\text{C}) = 79.1$ ppm), originating from the imine N=CH, (ii) two signals at $\delta = 0.42$ and 0.14 ppm that are

diastereotopic methylene protons on the same carbon ($\delta(^{13}\text{C}) = 29.7$ ppm),¹⁷ and (iii) two SiMe_3 signals at $\delta = -0.14$ and -0.52 ppm ($\delta(^{13}\text{C}) = 1.7$ and -1.9 ppm, respectively).¹⁸ The methylene protons each couple to the methine proton, in addition to coupling to each other, making each signal an approximate doublet of doublets, which is expected for the ABX spin system.¹² Although this species could not be isolated from the complex mixture, additional evidence for this transformation is found by analyzing the organic products after protonolysis with MeOH by mass spectroscopy: two major peaks in the electrospray negative ion mode spectrum ($m/z = 450$ and 538) correspond to $(\text{FI})^-$ and $(\text{FI}-\text{CH}_2\text{SiMe}_3)\text{H}^-$, respectively. Also the EPR spectrum (see above) exhibits a shoulder slightly downfield of the main signal at $g \approx 1.960$, indicating the formation of another Ti^{III} species, suggesting that both the active catalyst and $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2]^+$ are reduced *in situ*. This side reaction may account for the lower ethylene trimerization activity for $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2]^+$ compared with $[(\text{FI})\text{TiMe}_2]^+$.¹⁹

3. Activation and Catalysis with $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$.

Unlike $(\text{FI})\text{TiMe}_3$ and $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$, no titanium complex can be detected by ^1H NMR spectroscopy from the reaction between $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in $\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{F}_2$ (ca. 0.65 mL, 0.05 mL) at room temperature; EPR spectroscopy indicates that one major Ti^{III} species is produced ($g = 1.976$). If, however, the reaction is carried out at -78°C and allowed to warm to -20°C in the probe of the NMR spectrometer using a $\text{C}_7\text{D}_8/o\text{-C}_6\text{H}_4\text{F}_2$ (ca. 0.65 mL, 0.05 mL) solvent mixture, the ^1H , ^{13}C ,¹⁷ and ^{19}F NMR spectroscopic features expected for $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2][\text{MeB}(\text{C}_6\text{F}_5)_3]$ can be observed (Scheme 5). As with $[(\text{FI})\text{TiMe}_2]^+$ and $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2]^+$, they indicate OMe coordination to Ti, chemically inequivalent neopentyl (CH_2CMe_3) groups, and a non-coordinated solvent-separated anion $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$.⁷ Addition of ethylene (1 atm) at -20°C to this solution of $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$ results in catalytic trimerization with production of 1-hexene (Scheme 5).

Scheme 5.

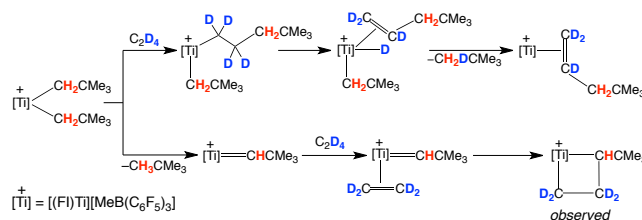


The ^1H NMR spectrum also shows evidence for a new diamagnetic titanium species which exhibits, in addition to a set of (FI) signals, five chemically inequivalent signals corresponding to two methylenes (CH_2) and one methine (CH), and one *tert*-butyl resonance, based on ^1H , COSY, TOCSY, HSQC and HMBC spectroscopies. These data could be consistent with a Ti^{II} -neohexene ($\text{H}_2\text{C}=\text{CHCH}_2\text{CMe}_3$) adduct, formed by the initiation pathway of

Scheme 1: ethylene insertion, β -H elimination and reductive elimination of neopentane (CMe_4). However, this hypothesis is ruled out by a parallel experiment using ethylene- d_4 : of the five new ^1H NMR signals seen with C_2H_4 , only the methine peak remains with C_2D_4 ; the neohexene, $\text{D}_2\text{C}=\text{CDCH}_2\text{CMe}_3$, should show the two methylene signals instead (Scheme 6, top). Instead, we propose that the new species is the titanacyclobutane $[(\text{FI})\text{Ti}(\text{CH}(\text{CMe}_3)\text{CH}_2\text{CH}_2)]^+$, resulting from $[2+2]$ cycloaddition of ethylene with a transient neopentylidene, $[(\text{FI})\text{Ti}(=\text{CHCMe}_3)]^+$; the isotopologue obtained with ethylene- d_4 would be expected to give the observed single ^1H NMR peak (Scheme 6, bottom).²⁰ A number of titanacyclobutane complexes, typically formed from an alkylidene and olefin, have been reported previously.^{21–29}

Analysis by GC/MS³⁰ of the neopentane generated in the above experiment, carried out under an atmosphere of ethylene- d_4 , indicates formation of a $\sim 1:1$ mixture of neopentane- d_1 and neopentane- d_0 . This is the expected result if generation of the active trimerization catalyst by the mechanism (Scheme 1; Scheme 6, top) previously proposed for $(\text{FI})\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ proceeds at a comparable rate with competitive α -abstraction (Scheme 6, bottom). Furthermore, $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}/\text{B}(\text{C}_6\text{F}_5)_3$ under an atmosphere of ethylene gives the same major Ti^{III} species (isotropic g value of 1.958) observed for both $(\text{FI})\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ and $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}/\text{B}(\text{C}_6\text{F}_5)_3$ (see above). All observations are thus consistent with a common mechanism for initiation.

Scheme 6.



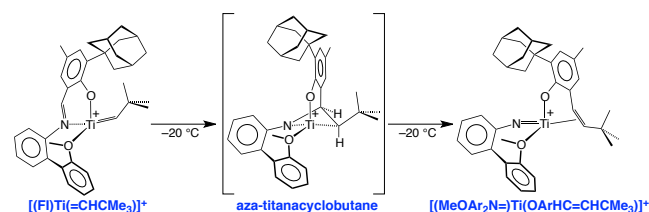
In an attempt to observe the proposed neopentylidene, we examined the reactivity of $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$ at low temperature in the absence of ethylene. Indeed, a solution of $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$ in $\text{C}_7\text{D}_8/o\text{-C}_6\text{H}_4\text{F}_2$ (ca. 0.65 mL/0.05 mL) at -30°C is not stable; it converts to the neopentylidene complex $[(\text{FI})\text{Ti}(=\text{CHCMe}_3)]^+$ by α -elimination of CMe_4 over a period of one day (Scheme 5). Characteristic NMR spectroscopic features of the $\text{Ti}=\text{CHCMe}_3$ fragment are ^1H and ^{13}C signals at $\delta = 9.91$ ppm and 310.9 ppm respectively, and a $^1\text{J}_{\text{C-H}}$ coupling constant of 96 Hz,³¹ similar to other reported titanium alkylidenes.^{23,32–36} Addition of C_2H_4 or C_2D_4 (1 atm) at -20°C to the solution of $[(\text{FI})\text{Ti}(=\text{CHCMe}_3)]^+$ immediately produces the ^1H NMR signals assigned to $[(\text{FI})\text{Ti}(\text{CH}(\text{CMe}_3)\text{CH}_2\text{CH}_2)]^+$ or $[(\text{FI})\text{Ti}(\text{CH}(\text{CMe}_3)\text{CD}_2\text{CD}_2)]^+$ (Scheme 5), with complete disappearance of the signals for $[(\text{FI})\text{Ti}(=\text{CHCMe}_3)]^+$. The ^{13}C NMR chemical shifts (α -C's: 99.2 and 164.5 ppm; β -C: 6.8 ppm) are similar to those of other titanacyclobutane complexes, which exhibit upfield β -C signals.^{21–28} For example, $\text{Cp}_2\text{Ti}(\text{CH}_2\text{CH}(\text{CHMe}_2)\text{CH}_2)$ has ^{13}C NMR chemical shifts of 75.2 ppm and 13.2 ppm (α and β respectively).²¹

It is important to note that significantly less 1-hexene is produced when $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$ is allowed to convert partially to $[(\text{FI})\text{Ti}(=\text{CHCMe}_3)]^+$ before addition of ethylene than when

ethylene is added immediately after it is generated.³⁸ This suggests that $[(\text{FI})\text{Ti}(\text{=CHCMe}_3)]^+$ and $[(\text{FI})\text{Ti}(\text{CH}(\text{CMe}_3)\text{CH}_2\text{CH}_2)]^+$ are *not* intermediates or precursors for catalytic ethylene trimerization, but rather off-cycle species that lead to decomposition.

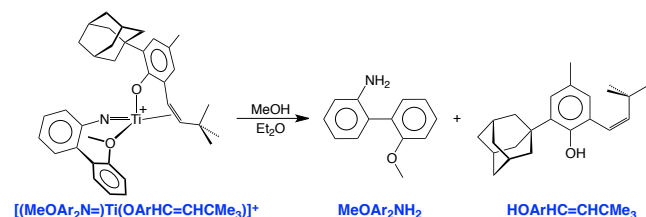
To further complicate matters, $[(\text{FI})\text{Ti}(\text{=CHCMe}_3)]^+$ is also not stable in solution; over a period of hours at -20°C , it converts to a new species that we assign as the imido-olefin complex $[(\text{MeOAr}_2\text{N=})\text{Ti}(\text{OArHC=CHCMe}_3)]^+$. ^1H NMR spectroscopic features that support this assignment are the loss of the (FI) imine (N=CH) signal, and the appearance of two olefinic methine CH signals at $\delta = 4.72$ and 4.98 ppm, with ^{13}C NMR chemical shifts of 144.5 and 123.3 ppm, respectively. Such a product could form by an intramolecular metathesis reaction between the neopentylidene and imine of the (FI) ligand (Scheme 7); similar transformations have been observed previously by Mindiola and coworkers, employing a $(\text{nacnac})\text{Ti}(\text{=CHCMe}_3)(\text{OTf})$ complex.^{32,39} While the putative intermediate in this sequence, the aza-titanacyclobutane complex^{40–45} shown in Scheme 7, might also be consistent with the NMR observations, important evidence for the proposed assignment was obtained by treating the new species with MeOH. Protonolysis of $[(\text{MeOAr}_2\text{N=})\text{Ti}(\text{OArHC=CHCMe}_3)]^+$ would be expected to give two organic fragments, $\text{MeOAr}_2\text{NH}_2$ and HOArHC=CHCMe_3 (Scheme 8), and both were obtained as major products, confirmed by comparison with a pure sample or by ^1H , ^{13}C , HSQC and HMBC spectroscopies respectively, along with GC/MS for both (m/z of 199.1 and 324.3). The olefin in HOArHC=CHCMe_3 is the *Z* isomer, based on the characteristically small three bond coupling constant ($^3J_{\text{H-H}} = 12$).⁴⁶

Scheme 7.



After establishing the above transformations by low temperature NMR spectroscopy, we reexamined the room temperature reaction of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in $\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{F}_2$. Analysis of the organic material after treatment with MeOH by GC/MS gave the same two major peaks (m/z of 199.1 and 324.3), demonstrating that the same fragmentation occurs at room temperature. Additionally, the Ti^{III} species with the isotropic g value of 1.976 (see above) can be observed by room temperature EPR spectroscopy after carrying out reactions at low temperature. This species therefore might be the neutral complex $[(\text{MeOAr}_2\text{N=})\text{Ti}^{\text{III}}(\text{OArHC=CHCMe}_3)]$, perhaps with solvent or another L-type ligand coordinated to Ti, although we have no definite evidence on its structure at this time.

Scheme 8.



Whereas the cation formed from $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in C_6D_6 is extremely unstable at room temperature, decomposing in less than 1 minute, a solution of the neutral precursor $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ in C_6D_6 decomposes much more slowly, over a period of hours at 25°C . Analysis of the resulting solution by EPR spectroscopy shows the Ti^{III} species with an isotropic g value of 1.976 , and after treatment with MeOH, analysis by GC/MS shows two major peaks with m/z of 199.1 and 324.3 . These observations taken together show that $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ converts to the same Ti^{III} species as does $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$, $[(\text{MeOAr}_2\text{N=})\text{Ti}^{\text{III}}(\text{OArHC=CHCMe}_3)]$. It thus appears that the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ in effect accelerates formation of the neopentylidene. This stands in contrast to behavior typically observed in the literature: α -hydrogen elimination is more commonly promoted by bulky Lewis bases (e.g., phosphines), heat, light, Brønsted bases or oxidants.^{31,36,47}

As noted earlier, even with all of these side reactions competing, the combination of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ still generates a species capable of catalytically trimerizing ethylene and α -olefins. When a solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ ($7\ \mu\text{mol}$, $7\ \text{mM}$) in $o\text{-C}_6\text{H}_4\text{F}_2$ ($1\ \text{mL}$) is first saturated with ethylene ($1\ \text{atm}$) and then treated with one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ while still under a constant pressure of ethylene at 25°C , 1-hexene and C_{10} olefins are rapidly produced, with the same distribution as $(\text{FI})\text{TiMe}_3$ and $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$, and only trace amounts of polyethylene ($< 3\ \text{mg}$). Remarkably, although this system gave less product than the other two (TON ca. 2.5×10^3), that degree of conversion was complete after only 20 minutes (by which time activity had completely ceased), whereas $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$ and $(\text{FI})\text{TiMe}_3$ required three hours to go to completion. In fact, if the same procedure is repeated at -20°C for 3 hours, a TON of 8.9×10^3 is achieved, which is the highest for this series of precatalysts thus far. The $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}/\text{B}(\text{C}_6\text{F}_5)_3$ system is clearly *more* active than the other two (Table 2), reflecting the faster rate of initiation (by at least an order of magnitude) for $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$ compared with $[(\text{FI})\text{TiMe}_2]^+$ and $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2]^+$.

The faster rate of initiation is also apparent for α -olefin oligomerization with $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$. When a solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ in 1-pentene is activated with $\text{B}(\text{C}_6\text{F}_5)_3$, trimerization catalysis proceeds rapidly (Scheme 4) and is complete after only 20 minutes with a TON of ca. 500. In contrast, when 1-pentene oligomerization with $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}/\text{B}(\text{C}_6\text{F}_5)_3$ is analyzed after 20 minutes, negligible quantities of trimers are observed. Like $(\text{FI})\text{TiMe}_3$ and $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$, the oligomer selectivity is greater than 95% for trimers, and 85% of the trimers are one regioisomer (Scheme 4), further demonstrating that all three precatalysts produce the same active species.

CONCLUSIONS

Both of the two new phenoxy-imine Ti complexes synthesized here, $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$ and $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$, generate olefin trimerization catalysts upon activation with a stoichiometric amount of $\text{B}(\text{C}_6\text{F}_5)_3$, with selectivities virtually identical to those previously obtained with $(\text{FI})\text{TiMe}_3$, strongly suggesting that the active species is the same in the three systems. Whereas trimerization catalysis proceeds at about the same rate starting with $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2]^+$ or $[(\text{FI})\text{TiMe}_2]^+$, it is significantly faster for $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$, suggesting that the initial goal of accelerating initiation was achieved for the case of neopentyl. For $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$ side reactions are

Table 3. Crystal, intensity collection, and refinement data.

	(FI)Ti(CH ₂ SiMe ₃) ₂ Cl ^a	(FI)Ti(CH ₂ SiMe ₃) ₂ Me ^b	(FI)Ti(CH ₂ CMe ₃) ₂ Cl ^b	(FI)Ti(CH ₂ CMe ₃) ₂ Me
lattice	Monoclinic	Triclinic	Triclinic	Monoclinic
formula	C ₄₃ H ₆₄ ClNO ₃ Si ₂ Ti	C ₄₅ H ₆₉ NO ₃ Si ₂ Ti	C ₄₆ H ₆₆ ClNO ₂ Ti	C ₄₂ H ₅₇ NO ₂ Ti
formula weight	782.48	760.09	748.34	655.78
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.2620(3)	9.6385(5)	12.1256(9)	9.5811(12)
<i>b</i> /Å	22.4163(9)	11.1526(6)	12.3667(10)	20.012(3)
<i>c</i> /Å	21.2155(8)	20.9436(12)	14.8256(11)	19.283(2)
α/°	90	97.266(3)	92.283(4)	90
β/°	95.996(2)	97.906(3)	94.294(4)	101.171(4)
γ/°	90	100.804(3)	106.191(4)	90
<i>V</i> /Å ³	4380.7(3)	2163.4(2)	2124.7(3)	3627.2(8)
<i>Z</i>	4	2	2	4
temperature (K)	100(2)	100(2)	100(2)	100(2)
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.186	1.167	1.170	1.201
μ (Mo Kα), mm ⁻¹	0.348	0.289	0.301	0.272
θ max, deg.	35.361	33.142	41.154	28.095
no. of data collected	166156	97117	154696	61492
no. of data	20105	16165	28144	8174
no. of parameters	486	487	486	440
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0535	0.0469	0.0521	0.0529
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1353	0.1145	0.1329	0.1008
<i>R</i> ₁ [all data]	0.0756	0.0744	0.0900	0.1128
<i>wR</i> ₂ [all data]	0.1472	0.1280	0.1548	0.1195
GOF	1.065	1.023	1.025	1.016

^a Crystallized with one molecule of Et₂O in the asymmetric unit. ^b Crystallized with one molecule of pentane in the asymmetric unit.

rapid as well: it first undergoes α-elimination to the neopentylidene complex [(FI)Ti(=CHCMe₃)]⁺, which in turn leads to the titanacyclobutane complex [(FI)Ti(CH(CMe₃)CH₂CH₂)]⁺ or the imido-olefin complex [(MeOAr₂N=)Ti(OArHC=CHCMe₃)]⁺ in the presence or absence of ethylene respectively. Unfortunately, none of these species appears to participate in trimerization catalysis, so the higher catalytic activity is offset by the lower catalyst stability. Ongoing work is aimed at determining whether a suitable combination of ligands and conditions can give the desired fast initiation and consequent higher catalytic activity without sacrificing catalyst stability.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed using glovebox, high-vacuum, and/or Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.⁴⁸ Solvents were purified and degassed by using standard procedures. NMR spectra were acquired at 25 °C, unless otherwise specified, and measured on Varian spectrometers at field strengths of 300 MHz, 400 MHz, 500 MHz and 600 MHz. ¹H chemical shifts are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C₆D₅H, δ 7.14 for C₆D₄HCl, δ 6.97 for C₇D₇H).⁴⁹ ¹³C chemical shift are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the solvent (δ 128.06 for C₆D₆, δ 134.19 for C₆D₅Cl, δ 128.87 for C₇D₈).⁴⁹ ¹³C chemical shift for all cationic complexes in this report were determined by 2D HSQC and HMBC spectroscopies. Coupling constants are given in Hz. ¹⁹F chemical shifts are reported in ppm relative to the absolute ¹H chemical shift reference. NMR spectra for (FI)Ti(CH₂SiMe₃)₂Cl, (FI)Ti(CH₂SiMe₃)₂Me, (FI)Ti(CH₂CMe₃)₂Cl, (FI)Ti(CH₂CMe₃)₂Me and selected reaction mixtures are shown in

the Supporting Information. X-band EPR spectra were acquired at room temperature on a Bruker EMX spectrometer. 1,4-Dioxane, *o*-C₆H₄F₂, and 1-pentene 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. C₆D₆, C₇D₈, and C₆D₅Cl were dried over molecular sieves (3 Å) for at least two days prior to use. Me₃SiCH₂MgCl and Me₃CCH₂MgCl were purchased from Aldrich as 1.0 M solutions in Et₂O. (FI)TiCl₃ was synthesized by our modified⁷ literature method.⁵

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 3. 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 2014/2).⁵⁰

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 from reference 7 were used. 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 (FI)Ti(CH₂SiMe₃)₂Cl. A solution of Me₃SiCH₂MgCl in Et₂O (0.41 mL, 1M, 0.41 mmol) was added to a stirring suspension of (FI)TiCl₃ (100 mg, 0.17 mmol) in Et₂O (5 mL) cooled to -30 °C, and was stirred for 5 minutes while warming. After this period, 1,4-dioxane (~0.05 mL, 0.6 mmol) was added, causing a precipitate to form, and the volatiles were removed *in vacuo*. The solid was extracted with pentane (2 × 5 mL), filtered through celite, and concentrated to ~1 mL causing crystals to form. The mixture was cooled at -30 °C for several days, thereby depositing yellow crystals

which were isolated, washed with cold pentane ($-30\text{ }^{\circ}\text{C}$, $\sim 0.5\text{ mL}$), and dried *in vacuo* to give (FI)Ti(CH₂SiMe₃)₂Cl as a yellow crystalline solid (70 mg, 60% yield). X-ray quality crystals were obtained by cooling a solution of (FI)Ti(CH₂SiMe₃)₂Cl in Et₂O/pentane (1:1) at $-30\text{ }^{\circ}\text{C}$. Anal. calcd. for (FI)Ti(CH₂SiMe₃)₂Cl: C, 66.1%; H, 7.7%; N, 2.0%. Found: C, 65.5%; H, 7.2%; N, 1.8%. ¹H NMR (C₆D₆): 0.03 [br s, 9H of Ti(CH₂SiMe₃)₂], 0.25 [br s, 1H of Ti(CH₂SiMe₃)₂], 0.34 [br s, 9H of Ti(CH₂SiMe₃)₂], 1.81 [d, AB pattern, ²J_{H-H} = 12, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 1.92 [d, AB pattern, ²J_{H-H} = 12, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 2.17 [s, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 2.17 [s, 3H of ArMe], 2.45 [s, 6H of C(CH₂)₃(CH)₃(CH₂)₃], 2.83 [br s, 3H of OMe], 2.99 [br s, 1H of Ti(CH₂SiMe₃)₂], 3.15 [br s, 1H of Ti(CH₂SiMe₃)₂], 3.74 [br s, 1H of Ti(CH₂SiMe₃)₂], 6.15 [br s, 1H of Ar], 6.71 [s, 1H of Ar], 6.91 [br s, 2H of Ar], 7.02 [d, ³J_{H-H} = 8, 1H of Ar], 7.13 [t, ³J_{H-H} = 8, 1H of Ar], 7.20 [m, 2H of Ar], 7.35 [s, 1H of Ar], 7.61 [br s, 1H of Ar], 8.52 [s, 1H of N=CH]. ¹³C{¹H} NMR (C₆D₆): 1.9 [br s, 6C of Ti(CH₂SiMe₃)₂], 20.8 [s, 1C of ArMe], 29.5 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 37.3 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 37.6 [s, 1C of C(CH₂)₃(CH)₃(CH₂)₃], 41.4 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 54.5 [s, 1C of OMe], 102.4 [very br, 2C of Ti(CH₂SiMe₃)₂], 110.3 [s, 1CH of Ar], 121.8 [s, 1CH of Ar], 123.3 [s, 1CH of Ar], 124.2 [s, 1C of Ar], 126.8 [s, 1CH of Ar], 128.5 [s, 1CH of Ar], 128.7 [s, 1C of Ar], 129.1 [s, 1C of Ar], 129.6 [s, 1CH of Ar], 131.7 [s, 1CH of Ar], 133.1 [s, 1CH of Ar], 133.4 [s, 1C of Ar], 134.3 [s, 1CH of Ar], 135.6 [s, 1CH of Ar], 139.1 [s, 1C of Ar], 156.0 [s, 1C of Ar], 156.7 [s, 1C of Ar], 161.2 [s, 1C of Ar], 173.0 [s, 1C of N=CH].

Synthesis of (FI)Ti(CH₂SiMe₃)₂Me. A solution of Me₃SiCH₂MgCl in Et₂O (0.82 mL, 1M, 0.82 mmol) was added to a stirring suspension of (FI)TiCl₃ (200 mg, 0.33 mmol) in Et₂O (7 mL) cooled to $-30\text{ }^{\circ}\text{C}$, and was stirred for 5 minutes while warming. The mixture was then cooled to $-30\text{ }^{\circ}\text{C}$ and treated with a solution of MeMgBr in Et₂O (0.26 mL, 3M, 0.78 mmol), and was then stirred at $0\text{ }^{\circ}\text{C}$ for 3.5 hours. After this period, 1,4-dioxane ($\sim 0.1\text{ mL}$, 1.2 mmol) was added, causing a precipitate to form, and the volatiles were removed *in vacuo* (once the sample is dry, the next steps should be done immediately as further evacuation at room temperature results in decomposition). The solid was extracted with pentane (5 mL, then 10 mL), filtered through a medium porosity frit with a 0.5 cm bed of celite, and the filtrate was concentrated to $\sim 2\text{ mL}$ causing crystals to form. The mixture was cooled at $-30\text{ }^{\circ}\text{C}$ for several days, thereby depositing yellow/orange crystals which were isolated, washed with cold pentane ($-30\text{ }^{\circ}\text{C}$, $\sim 1\text{ mL}$), and dried *in vacuo* to give (FI)Ti(CH₂SiMe₃)₂Me as a yellow/orange crystalline solid (134 mg, 59% yield). X-ray quality crystals were obtained by cooling a solution of (FI)Ti(CH₂SiMe₃)₂Me in pentane at $-30\text{ }^{\circ}\text{C}$. Anal. calcd. for (FI)Ti(CH₂SiMe₃)₂Me $\cdot 0.5(\text{C}_5\text{H}_{12})$: C, 70.5%; H, 8.8%; N, 1.9%. Found: C, 70.7%; H, 8.9%; N, 1.9%. ¹H NMR (C₆D₆): 0.17 [br s, 18H of Ti(CH₂SiMe₃)₂], 1.73 [s, 3H of TiMe], 1.81 [d, AB pattern, ²J_{H-H} = 12, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 1.93 [d, AB pattern, ²J_{H-H} = 12, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 2.18 [br s, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 2.20 [s, 3H of ArMe], 2.37 [br s, 6H of C(CH₂)₃(CH)₃(CH₂)₃], 2.91 [s, 3H of OMe], 6.22 [d, ³J_{H-H} = 8, 1H of Ar], 6.77 [d, ⁴J_{H-H} = 2, 1H of Ar], 6.82 [t, ³J_{H-H} = 7, 1H of Ar], 6.92 [dt, ³J_{H-H} = 2, ³J_{H-H} = 8, 1H of Ar], 7.03 [dd, ³J_{H-H} = 8, ⁴J_{H-H} = 1, 1H of Ar], 7.08 [dt, ⁴J_{H-H} = 1, ³J_{H-H} = 8, 1H of Ar], 7.16 [m, 1H of Ar], 7.19 [m, 1H of Ar], 7.23 [dd, ³J_{H-H} = 8, ⁴J_{H-H} = 1, 1H of Ar], 7.32 [d, ⁴J_{H-H} = 2, 1H of Ar], 8.55 [s, 1H of N=CH], 4H of Ti(CH₂SiMe₃)₂ not observed. ¹³C{¹H} NMR (C₆D₆): 2.1 [s, 6C of Ti(CH₂SiMe₃)₂], 20.9 [s, 1C of ArMe], 29.5 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 37.4 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 37.5 [s, 1C of C(CH₂)₃(CH)₃(CH₂)₃], 41.2 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 54.6 [s, 1C of OMe], 70.7 [s, 1C of TiMe], 95.4 [very br, 2C of Ti(CH₂SiMe₃)₂], 110.8 [s, 1CH of Ar], 121.6 [s, 1CH of Ar], 123.4 [s, 1C of Ar], 124.5 [s, 1CH of Ar], 126.4 [s, 1CH

of Ar], 127.5 [s, 1C of Ar], 128.5 [s, 1CH of Ar], 128.7 [s, 1C of Ar], 129.9 [s, 1CH of Ar], 132.1 [s, 1CH of Ar], 132.7 [br s, 1C of Ar], 133.0 [s, 1CH of Ar], 133.1 [s, 1CH of Ar], 135.0 [s, 1CH of Ar], 139.2 [s, 1C of Ar], 155.6 [s, 1C of Ar], 156.2 [s, 1C of Ar], 162.5 [s, 1C of Ar], 172.4 [s, 1C of N=CH].

Synthesis of (FI)Ti(CH₂CMe₃)₂Cl. A solution of Me₃CCH₂MgCl in Et₂O (0.41 mL, 1M, 0.41 mmol) was added to a stirring suspension of (FI)TiCl₃ (100 mg, 0.17 mmol) in Et₂O (5 mL) cooled to $-30\text{ }^{\circ}\text{C}$, and was stirred for 5 minutes while warming. After this period, 1,4-dioxane ($\sim 0.05\text{ mL}$, 0.6 mmol) was added, causing a precipitate to form, and the volatiles were removed *in vacuo*. The solid was extracted with pentane (2 \times 5 mL), filtered through celite, and concentrated to $\sim 1\text{ mL}$ causing crystals to form. The mixture was cooled at $-30\text{ }^{\circ}\text{C}$ for several days, thereby depositing orange crystals which were isolated, washed with cold pentane ($-30\text{ }^{\circ}\text{C}$, $\sim 0.5\text{ mL}$), and dried *in vacuo* to give (FI)Ti(CH₂CMe₃)₂Cl as an orange crystalline solid (37 mg, 33% yield). (FI)Ti(CH₂CMe₃)₂Cl is not thermally stable, darkening in color at room temperature, and should therefore be stored at low temperature ($-30\text{ }^{\circ}\text{C}$ for this work). X-ray quality crystals were obtained by cooling a solution of (FI)Ti(CH₂CMe₃)₂Cl in pentane at $-30\text{ }^{\circ}\text{C}$. Anal. calcd. for (FI)Ti(CH₂CMe₃)₂Cl: C, 72.8%; H, 8.1%; N, 2.1%. Found: C, 71.0%; H, 7.8%; N, 2.1%. ¹H NMR (C₆D₆): 0.98 [br s, 9H of Ti(CH₂CMe₃)₂], 1.04 [d, ²J_{H-H} = 10, 1H of Ti(CH₂CMe₃)₂], 1.12 [br s, 9H of Ti(CH₂CMe₃)₂], 1.81 [d, AB pattern, ²J_{H-H} = 12, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 1.94 [d, AB pattern, ²J_{H-H} = 12, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 2.16 [br s, 3H of C(CH₂)₃(CH)₃(CH₂)₃], 2.16 [s, 3H of ArMe], 2.48 [br s, 6H of C(CH₂)₃(CH)₃(CH₂)₃], 2.81 [d, ²J_{H-H} = 10, 1H of Ti(CH₂CMe₃)₂], 2.90 [s, 3H of OMe], 2.94 [d, ²J_{H-H} = 10, 1H of Ti(CH₂CMe₃)₂], 3.29 [d, ²J_{H-H} = 10, 1H of Ti(CH₂CMe₃)₂], 6.19 [d, ³J_{H-H} = 8, 1H of Ar], 6.73 [d, ⁴J_{H-H} = 1, 1H of Ar], 6.88 [t, ³J_{H-H} = 7, 1H of Ar], 6.92 [dt, ⁴J_{H-H} = 2, ³J_{H-H} = 8, 1H of Ar], 6.98 [dd, ³J_{H-H} = 8, ⁴J_{H-H} = 1, 1H of Ar], 7.13 [dt, ⁴J_{H-H} = 1, ³J_{H-H} = 8, 1H of Ar], 7.20 [dt, ⁴J_{H-H} = 1, ³J_{H-H} = 8, 1H of Ar], 7.24 [d, ³J_{H-H} = 8, 1H of Ar], 7.36 [d, ⁴J_{H-H} = 2, 1H of Ar], 7.61 [br d, ³J_{H-H} = 6, 1H of Ar], 8.63 [s, 1H of N=CH]. ¹³C{¹H} NMR (C₆D₆): 20.8 [s, 1C of ArMe], 29.6 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 33.3 [br s, 6C of Ti(CH₂CMe₃)₂], 37.4 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 37.6 [s, 1C of C(CH₂)₃(CH)₃(CH₂)₃], 37.7 [br s, 2C of Ti(CH₂CMe₃)₂], 41.7 [s, 3C of C(CH₂)₃(CH)₃(CH₂)₃], 54.6 [s, 1C of OMe], 110.3 [s, 1CH of Ar], 115.6 [very br, 2C of Ti(CH₂CMe₃)₂], 121.9 [s, 1CH of Ar], 123.8 [s, 1CH of Ar], 124.3 [s, 1C of Ar], 126.7 [s, 1CH of Ar], 128.0 [s, 1C of Ar, located using 2D HMBC], 128.3 [s, 1C of Ar, located using 2D HMBC], 128.8 [s, 1CH of Ar], 129.4 [s, 1CH of Ar], 132.0 [s, 1CH of Ar], 133.2 [s, 1CH of Ar], 133.2 [s, 1C of Ar], 134.0 [s, 1CH of Ar], 135.7 [s, 1CH of Ar], 139.4 [s, 1C of Ar], 156.1 [s, 1C of Ar], 156.9 [s, 1C of Ar], 161.8 [s, 1C of Ar], 173.3 [s, 1C of N=CH].

Synthesis of (FI)Ti(CH₂CMe₃)₂Me. A solution of Me₃CCH₂MgCl in Et₂O (0.82 mL, 1M, 0.82 mmol) was added to a stirring suspension of (FI)TiCl₃ (200 mg, 0.33 mmol) in Et₂O (7 mL) cooled to $-30\text{ }^{\circ}\text{C}$, and was stirred for 5 minutes while warming. The mixture was then cooled to $-30\text{ }^{\circ}\text{C}$ and treated with a solution of MeMgBr in Et₂O (0.26 mL, 3M, 0.78 mmol), and was then stirred at $0\text{ }^{\circ}\text{C}$ for 3.5 hours. After this period, 1,4-dioxane ($\sim 0.1\text{ mL}$, 1.2 mmol) was added, causing a precipitate to form, and the volatiles were removed *in vacuo* (once the sample is dry, the next steps should be done immediately as further evacuation at room temperature results in decomposition). The solid was extracted with pentane (5 mL, then 10 mL), filtered through a medium porosity frit with a 0.5 cm bed of celite, and the filtrate was concentrated to $\sim 2\text{ mL}$ causing crystals to form. The mixture was cooled at $-30\text{ }^{\circ}\text{C}$ for several days, thereby depositing orange crystals which were isolated, washed with cold pentane ($-30\text{ }^{\circ}\text{C}$, $\sim 1\text{ mL}$), and dried *in vacuo* to give (FI)Ti(CH₂CMe₃)₂Me as an orange crystalline solid (96 mg, 44% yield). (FI)Ti(CH₂CMe₃)₂Me

is not thermally stable in the solid state or solution, darkening in color at room temperature, and should therefore be stored at low temperature ($-30\text{ }^{\circ}\text{C}$ for this work). Solutions of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ in C_6D_6 decompose over a period of hours to give a Ti^{III} species with an isotropic g value of 1.976 at room temperature. X-ray quality crystals were obtained by cooling a solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ in pentane at $-30\text{ }^{\circ}\text{C}$. ^1H NMR (C_6D_6): 1.07 [br s, 18H of $\text{Ti}(\text{CH}_2\text{CMe}_3)_2$], 1.78 [s, 3H of TiMe], 1.81 [d, AB pattern, $^2J_{\text{H-H}} = 12$, 3H of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 1.94 [d, AB pattern, $^2J_{\text{H-H}} = 12$, 3H of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 2.16 [br s, 3H of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 2.20 [s, 3H of ArMe], 2.39 [br s, 6H of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 2.93 [s, 3H of OMe], 6.25 [d, $^3J_{\text{H-H}} = 8$, 1H of Ar], 6.78 [d, $^4J_{\text{H-H}} = 2$, 1H of Ar], 6.82 [br t, $^2J_{\text{H-H}} = 7$, 1H of Ar], 6.93 [m, 1H of Ar], 7.02 [dd, $^3J_{\text{H-H}} = 8$, $^4J_{\text{H-H}} = 1$, 1H of Ar], 7.09 [dt, $^4J_{\text{H-H}} = 1$, $^3J_{\text{H-H}} = 8$, 1H of Ar], 7.16 [m, 1H of Ar], 7.21 [br d, $^3J_{\text{H-H}} = 7$, 1H of Ar], 7.27 [br d, $^3J_{\text{H-H}} = 7$, 1H of Ar], 7.32 [d, $^4J_{\text{H-H}} = 2$, 1H of Ar], 8.62 [s, 1H of $\text{N}=\text{CH}$], 4H of $\text{Ti}(\text{CH}_2\text{CMe}_3)_2$ not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 20.8 [s, 1C of ArMe], 29.5 [s, 3C of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 33.7 [s, 6C of $\text{Ti}(\text{CH}_2\text{CMe}_3)_2$], 37.4 [s, 2C of $\text{Ti}(\text{CH}_2\text{CMe}_3)_2$], 37.4 [s, 1C of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 37.5 [s, 3C of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 41.4 [s, 3C of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 54.6 [s, 1C of OMe], 71.7 [s, 1C of TiMe], 110.6 [s, 1CH of Ar], 111.8 [s, 2C of $\text{Ti}(\text{CH}_2\text{CMe}_3)_2$], 121.7 [s, 1CH of Ar], 123.7 [s, 1C of Ar], 124.4 [s, 1CH of Ar], 126.3 [s, 1CH of Ar], 127.0 [s, 1C of Ar], 128.1 [s, 1CH of Ar , located using 2D HSQC], 128.5 [s, 1C of Ar , located using 2D HMBC], 129.7 [s, 1CH of Ar], 132.1 [s, 1CH of Ar], 132.9 [s, 1C of Ar], 133.1 [s, 1CH of Ar], 133.3 [s, 1CH of Ar], 135.2 [s, 1CH of Ar], 139.4 [s, 1C of Ar], 156.1 [s, 1C of Ar], 156.2 [s, 1C of Ar], 162.8 [s, 1C of Ar], 172.5 [s, 1C of $\text{N}=\text{CH}$].

Reaction between $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$ and $\text{B}(\text{C}_6\text{F}_5)_3$. A light yellow solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$ (6 mg, 0.009 mmol) in a mixture of C_6D_6 (ca. 0.65 mL) and $o\text{-C}_6\text{H}_4\text{F}_2$ (ca. 0.05 mL) in an NMR tube equipped with a J. Young valve was treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (5 mg, 0.01 mmol) at room temperature, resulting in an immediate color change to yellow/orange. The sample was analyzed by ^1H , ^{19}F , COSY, HSQC and HMBC NMR spectroscopies, thereby demonstrating conversion to $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (ca. 80% by ^1H NMR integration). ^1H NMR ($\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{F}_2$): -0.50 [s, 9H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], -0.24 [s, 9H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 1.29 [br s, 3H of $\text{MeB}(\text{C}_6\text{F}_5)_3$], 1.82 [br s, 6H of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 2.05 [s, 3H of ArMe], 2.14 [s, 3H of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 2.24 [s, 6H of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 2.52 [d, $^2J_{\text{H-H}} = 11$, 1H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 3.18 [AB quartet, $^2J_{\text{H-H}} = 11$, 2H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 3.34 [d, $^2J_{\text{H-H}} = 11$, 1H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 3.89 [s, 3H of OMe], 6.30 [d, $^3J_{\text{H-H}} = 8$, 1H of Ar], 6.67 [s, 1H of Ar , located by COSY], 7.08 [m, 4H of Ar], 7.17 [m, 2H of Ar], 7.25 [t, $^3J_{\text{H-H}} = 8$, 1H of Ar], 7.34 [s, 1H of Ar], 7.77 [s, 1H of $\text{N}=\text{CH}$]. Selected $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{F}_2$): 1.3 [3C of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 1.4 [3C of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 11.3 [1C of $\text{MeB}(\text{C}_6\text{F}_5)_3$], 20.2 [1C of ArMe], 29.0 [3C of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 36.8 [3C of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 41.8 [3C of $\text{C}(\text{CH}_3)_3(\text{CH})_3(\text{CH}_2)_3$], 72.1 [1C of OMe], 109.2 [1C of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 110.7 [1C of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 174.5 [1C of $\text{N}=\text{CH}$]. ^{19}F NMR ($\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{F}_2$): -166.9 [t, $^3J_{\text{F-F}} = 20$, 6F of $\text{MeB}(\text{C}_6\text{F}_5)_3$, *para*-F], -164.4 [t, $^3J_{\text{F-F}} = 21$, 3F of $\text{MeB}(\text{C}_6\text{F}_5)_3$, *meta*-F], -131.7 [d, $^3J_{\text{F-F}} = 21$, 6F of $\text{MeB}(\text{C}_6\text{F}_5)_3$, *ortho*-F].

The solution described above was monitored over time, demonstrating conversion to $[(\text{FI-CH}_2\text{SiMe}_3)\text{Ti}(\text{CH}_2\text{SiMe}_3)]^+$. The sample was then treated with MeOH (ca. 0.1 mL), filtered and analyzed by several MS techniques including FAB, positive-ion mode electrospray, and negative-ion mode electrospray, all giving m/z consistent with $(\text{FI})\text{H}$ and $(\text{FI-CH}_2\text{SiMe}_3)_2$. Selected ^1H NMR ($\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{F}_2$): -0.52 [s, 9H of $(\text{FI-CH}_2\text{SiMe}_3)_2$], -0.14 [s, 9H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 0.13 [dd, $^2J_{\text{H-H}} = 14$, $^3J_{\text{H-H}} = 4$, 1H of $(\text{N-ArCH-CH}_2\text{SiMe}_3)_2$], 0.42 [dd, $^2J_{\text{H-H}}$

$= 14$, $^3J_{\text{H-H}} = 10$, 1H of $(\text{N-ArCH-CH}_2\text{SiMe}_3)_2$], 2.36 [d, $^2J_{\text{H-H}} = 10$, 1H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 2.66 [d, $^2J_{\text{H-H}} = 10$, 1H of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 3.45 [s, 3H of OMe], 4.15 [dd, $^3J_{\text{H-H}} = 11$, $^3J_{\text{H-H}} = 4$, 1H of $(\text{N-ArCH-CH}_2\text{SiMe}_3)_2$]. Selected $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6/o\text{-C}_6\text{H}_4\text{F}_2$): -1.9 [3C of $(\text{FI-CH}_2\text{SiMe}_3)_2$], 1.7 [3C of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$], 29.7 [1C of $(\text{N-ArCH-CH}_2\text{SiMe}_3)_2$], 70.5 [1C of OMe], 79.1 [1C of $(\text{N-ArCH-CH}_2\text{SiMe}_3)_2$], 105.7 [1C of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$].

Ethylene Trimerization Catalysis with $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$. (i) A solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$ (6 mg, 0.009 mmol) in a mixture of C_6D_6 (ca. 0.65 mL) and $o\text{-C}_6\text{H}_4\text{F}_2$ (ca. 0.05 mL) in an NMR tube equipped with a J. Young valve was treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (5 mg, 0.01 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 $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2][\text{MeB}(\text{C}_6\text{F}_5)_3]$. The solution was frozen, degassed, allowed to warm to room temperature, saturated with ethylene (1 atm), shaken to promote mixing, and continually re-saturated with ethylene until catalytic activity terminated. The sample was periodically analyzed by ^1H NMR spectroscopy, demonstrating the catalytic production of 1-hexene and slow disappearance of $[(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2]^+$. The solution was also analyzed by EPR spectroscopy, indicating the formation of a major Ti^{III} species, with an isotropic g value of 1.958 at room temperature, which increased intensity over the time course of the reaction. (ii) In a typical experiment, a solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$ (6 mg, 0.009 mmol) in $o\text{-C}_6\text{H}_4\text{F}_2$ (1 mL) in a 15 mL ampoule was treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (5 mg, 0.01 mmol) at room temperature. The solution was frozen, degassed, and allowed to warm to room temperature. The ampoule was then charged with ethylene (1 atm) and stirred for ca. 3 hours under constant ethylene pressure (1 atm) at room temperature. After this period, the volume of the solution had increased significantly (ca. 1 mL), but only a trace amount of polymer (< 3 mg) had formed. Adamantane was added as an internal integration standard, and the mixture was diluted with benzene, filtered through a plug of silica gel, and analyzed by GC. GC analysis demonstrated the catalytic production of 1-hexene, in addition to C_{10} olefins and C_{14} olefins, with a TON of ca. 4.1×10^3 mmol olefin oligomerized/mmol Ti.

1-Pentene Trimerization Catalysis with $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$. (i) In a typical experiment, a solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{SiMe}_3)_2\text{Me}$ (3 mg, 0.004 mmol) in 1-pentene (1 – 2 mL) was treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (2 mg, 0.004 mmol) at room temperature, and was stirred for ca. 12 hours. After this period, adamantane 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 demonstrated the formation of C_{15} olefins with a TON of ca. 900 mmol 1-pentene oligomerized/mmol Ti, with no other detectible oligomers. The C_{15} region of the gas chromatogram displayed one major peak ($\sim 85\%$), with two other minor peaks ($\sim 15\%$). (ii) When the above procedure was stirred for 20 minutes, GC analysis demonstrated negligible C_{15} production.

Reaction between $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ and $\text{B}(\text{C}_6\text{F}_5)_3$. (i) A light yellow/orange solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ (6 mg, 0.009 mmol) in a mixture of C_6D_6 (ca. 0.65 mL) and $o\text{-C}_6\text{H}_4\text{F}_2$ (ca. 0.05 mL) in an NMR tube equipped with a J. Young valve was treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (5 mg, 0.01 mmol) at room temperature, resulting in an immediate color change to orange. After ca. 1 minute, the solution color changed to dark brown and analysis by ^1H NMR spectroscopy gave no indication of any diamagnetic $(\text{FI})\text{Ti}$ species. The sample was analyzed by EPR spectroscopy, indicating the formation of a Ti^{III} species, with an isotropic g value of 1.976 at room temperature. The sample was then treated with MeOH (ca. 0.1 mL), filtered and analyzed by GC/MS giving two major organic fragments with m/z of 199.1 and 324.3. (ii) A light yellow/orange solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$

(6 mg, 0.009 mmol) in a mixture of C_7D_8 (ca. 0.65 mL) and $o\text{-}C_6H_4F_2$ (ca. 0.05 mL) or C_6D_5Cl (ca. 0.7 mL) was added to an NMR tube equipped with a J. Young valve. The sample was cooled at $-78^\circ C$, and then treated with $B(C_6F_5)_3$ (5 mg, 0.01 mmol), resulting in a color change to orange.⁵¹ The sample was allowed to warm to either $-30^\circ C$ or $-20^\circ C$ in the probe of the NMR spectrometer, and was analyzed by 1H , ^{19}F , COSY, HSQC and HMBC NMR spectroscopies, thereby demonstrating conversion to $[(FI)Ti(CH_2CMe_3)_2][MeB(C_6F_5)_3]$ (ca. 80% by 1H NMR integration). 1H NMR (C_6D_5Cl , $-20^\circ C$): 0.68 [s, 9H of $Ti(CH_2CMe_3)_2$], 0.80 [s, 9H of $Ti(CH_2CMe_3)_2$], 1.26 [br s, 3H of $MeB(C_6F_5)_3$], 1.63 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 1.83 [br s, 6H of $C(CH_2)_3(CH)_3(CH_2)_3$], 2.10 [s, 3H of $ArMe$], 2.13 [s, 3H of $C(CH_2)_3(CH)_3(CH_2)_3$], 2.27 [s, 6H of $C(CH_2)_3(CH)_3(CH_2)_3$], 2.74 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 2.90 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 2.97 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 4.22 [s, 3H of OMe], 6.51 [d, $^3J_{H-H} = 7$, 1H of Ar], 6.60 [br s, 1H of Ar], 7.21 [m, 3H of Ar], 7.26 [m, 2H of Ar], 7.35 [m, 2H of Ar], 7.45 [br s, 1H of Ar], 7.99 [s, 1H of $N=CH$]. Selected $^{13}C\{^1H\}$ NMR (C_6D_5Cl , $-20^\circ C$): 10.9 [1C of $MeB(C_6F_5)_3$], 20.0 [1C of $ArMe$], 28.6 [3C of $C(CH_2)_3(CH)_3(CH_2)_3$], 32.4 [3C of $Ti(CH_2CMe_3)_2$], 32.4 [3C of $Ti(CH_2CMe_3)_2$], 36.4 [3C of $C(CH_2)_3(CH)_3(CH_2)_3$], 41.5 [3C of $C(CH_2)_3(CH)_3(CH_2)_3$], 72.5 [1C of OMe], 121.2 [1C of $Ti(CH_2CMe_3)_2$], 130.5 [1C of $Ti(CH_2CMe_3)_2$], 173.8 [1C of $N=CH$]. Selected 1H NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$): 0.62 [s, 9H of $Ti(CH_2CMe_3)_2$], 0.67 [s, 9H of $Ti(CH_2CMe_3)_2$], 1.75 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 2.63 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 2.83 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 2.92 [d, $^2J_{H-H} = 11$, 1H of $Ti(CH_2CMe_3)_2$], 3.92 [s, 3H of OMe], 7.70 [s, 1H of $N=CH$]. Selected $^{13}C\{^1H\}$ NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$): 32.2 [3C of $Ti(CH_2CMe_3)_2$], 32.2 [3C of $Ti(CH_2CMe_3)_2$], 72.6 [1C of OMe], 174.0 [1C of $N=CH$]. ^{19}F NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-30^\circ C$): -166.6 [t, $^3J_{F-F} = 20$, 6F of $MeB(C_6F_5)_3$, *para*-F], -164.0 [t, $^3J_{F-F} = 21$, 3F of $MeB(C_6F_5)_3$, *meta*-F], -131.8 [d, $^3J_{F-F} = 21$, 6F of $MeB(C_6F_5)_3$, *ortho*-F].

Formation of $[(FI)Ti(=CHCMe_3)]^+$ and conversion to $[(MeOAr_2N=)Ti(OArHC=CHCMe_3)]^+$. A light yellow/orange solution of $(FI)Ti(CH_2CMe_3)_2Me$ (6 mg, 0.009 mmol) in a mixture of C_7D_8 (ca. 0.65 mL) and $o\text{-}C_6H_4F_2$ (ca. 0.05 mL) or C_6D_5Cl (ca. 0.7 mL) was added to a small vial and cooled at $-30^\circ C$. The sample was then treated with $B(C_6F_5)_3$ (5 mg, 0.01 mmol), resulting in a color change to orange, and stored in the vial at $-30^\circ C$ for ca. 1 day. The solution was then pipetted into an NMR tube equipped with a J. Young valve (which was pre-cooled to $< -78^\circ C$), sealed, and then cooled at $-78^\circ C$. The sample was allowed to warm to $-20^\circ C$ in the probe of the NMR spectrometer, and was analyzed by 1H , COSY, HSQC and HMBC NMR spectroscopies, thereby demonstrating formation of $[(FI)Ti(=CHCMe_3)]^+$. Selected 1H NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$): 0.72 [s, 9H of $Ti(=CHCMe_3)$], 3.49 [s, 3H of OMe], 7.75 [s, 1H of $N=CH$], 9.91 [s, 1H of $Ti(=CHCMe_3)$]. Selected $^{13}C\{^1H\}$ NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$): 30.3 [3C of $Ti(=CHCMe_3)$], 72.1 [1C of OMe], 168.6 [1C of $N=CH$], 311.0 [1C of $Ti(=CHCMe_3)$]. Selected 1H NMR (C_6D_5Cl , $-20^\circ C$): 0.72 [s, 9H of $Ti(=CHCMe_3)$], 4.05 [s, 3H of OMe], 8.15 [s, 1H of $N=CH$], 9.84 [s, 1H of $Ti(=CHCMe_3)$]. Selected $^{13}C\{^1H\}$ NMR (C_6D_5Cl , $-20^\circ C$): 312.3 [1C of $Ti(=CHCMe_3)$].

At $-20^\circ C$, $[(FI)Ti(=CHCMe_3)]^+$ converted to $[(MeOAr_2N=)Ti(OArHC=CHCMe_3)]^+$ over a period of hours, and was analyzed by 1H , COSY, HSQC and HMBC NMR spectroscopies. Selected 1H NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$): 0.76 [s, 9H of $Ti(ArHC=CHCMe_3)$], 3.61 [s, 3H of OMe], 4.72 [d, $^3J_{H-H} = 13$, 1H of $Ti(ArHC=CHCMe_3)$], 4.98 [d, $^3J_{H-H} = 13$, 1H of $Ti(ArHC=CHCMe_3)$]. Selected $^{13}C\{^1H\}$ NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$):

29.9 [3C of $Ti(ArHC=CHCMe_3)$], 72.1 [1C of OMe], 123.3 [1C of $Ti(ArHC=CHCMe_3)$], 144.5 [1C of $Ti(ArHC=CHCMe_3)$].

Isolation of $HOArHC=CHCMe_3$. A light yellow/orange solution of $(FI)Ti(CH_2CMe_3)_2Me$ (40 mg, 0.061 mmol) in Et_2O (ca. 3 mL) was added to a large vial and cooled at $-30^\circ C$. The sample was then treated with $B(C_6F_5)_3$ (40 mg, 0.078 mmol), resulting in a color change to orange, and stored in the vial at $-30^\circ C$ for ca. 4 days. After this period, the sample was treated with $MeOH$ (ca. 0.2 mL), filtered and analyzed by GC/MS giving two major organic fragments with m/z of 199.1 and 324.3. The volatile components were removed under reduced pressure, and $HOArHC=CHCMe_3$ was separated by flash column chromatography (silica gel, hexanes). 1H NMR of $HOArHC=CHCMe_3$ ($CDCl_3$): 0.95 [s, 9H of CMe_3], 1.77 [m, AB pattern, 6H of $C(CH_2)_3(CH)_3(CH_2)_3$], 2.06 [br s, 3H of $C(CH_2)_3(CH)_3(CH_2)_3$], 2.12 [br s, 6H of $C(CH_2)_3(CH)_3(CH_2)_3$], 2.25 [s, 3H of $ArMe$], 5.19 [s, 1H of $ArOH$], 5.92 [d, $^3J_{H-H} = 12$, 1H of $ArHC=CHCMe_3$], 6.14 [d, $^3J_{H-H} = 12$, 1H of $ArHC=CHCMe_3$], 6.70 [br s, 1H of Ar], 6.91 [br s, 1H of Ar]. $^{13}C\{^1H\}$ NMR of $HOArHC=CHCMe_3$ ($CDCl_3$): 21.0 [s, 1C of $ArMe$], 29.4 [s, 3C of $C(CH_2)_3(CH)_3(CH_2)_3$], 30.3 [s, 3C of CMe_3], 34.9 [s, 1C of CMe_3], 36.9 [s, 1C of $C(CH_2)_3(CH)_3(CH_2)_3$], 37.4 [s, 3C of $C(CH_2)_3(CH)_3(CH_2)_3$], 40.6 [s, 3C of $C(CH_2)_3(CH)_3(CH_2)_3$], 120.6 [s, 1C of $ArHC=CHCMe_3$], 125.6 [s, 1C of Ar], 126.3 [s, 1CH of Ar], 127.3 [s, 1CH of Ar], 128.2 [s, 1C of Ar], 135.4 [s, 1C of Ar], 148.9 [s, 1C of Ar], 149.2 [s, 1C of $ArHC=CHCMe_3$].

Formation of $[(FI)Ti(CH(CMe_3)CH_2CH_2)]^+$. A light yellow/orange solution of $(FI)Ti(CH_2CMe_3)_2Me$ (6 mg, 0.009 mmol) in a mixture of C_7D_8 (ca. 0.65 mL) and $o\text{-}C_6H_4F_2$ (ca. 0.05 mL), or C_6D_5Cl (ca. 0.7 mL) was added to an NMR tube equipped with a J. Young valve. The sample was cooled at $-78^\circ C$, and then treated with $B(C_6F_5)_3$ (5 mg, 0.01 mmol) and ethylene (1 atm), resulting in a color change to orange.⁵¹ The sample was allowed to warm to either $-30^\circ C$ or $-20^\circ C$ in the probe of the NMR spectrometer, and was analyzed by 1H , COSY, TOCSY, HSQC and HMBC NMR spectroscopies, thereby demonstrating the catalytic production of 1-hexene and the formation of $[(FI)Ti(CH(CMe_3)CH_2CH_2)]^+$. An analogous experiment was conducted with ethylene- d_4 , demonstrating formation of $[(FI)Ti(CH(CMe_3)CD_2CD_2)]^+$. Selected 1H NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$): 0.67 [s, 9H of $Ti(CH(CMe_3)CH_2CH_2)$], 1.01 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 2.88 [s, 3H of OMe], 3.29 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 3.49 [t, $^3J_{H-H} = 11$, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 3.82 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 4.56 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 7.79 [s, 1H of $N=CH$]. Selected $^{13}C\{^1H\}$ NMR ($C_7D_8/o\text{-}C_6H_4F_2$, $-20^\circ C$): 6.8 [1C of $Ti(CH(CMe_3)CH_2CH_2)$], 30.9 [3C of $Ti(CH(CMe_3)CH_2CH_2)$], 70.7 [1C of OMe], 99.2 [1C of $Ti(CH(CMe_3)CH_2CH_2)$], 164.5 [1C of $Ti(CH(CMe_3)CH_2CH_2)$], 174.4 [1C of $N=CH$]. Selected 1H NMR (C_6D_5Cl , $-20^\circ C$): 0.72 [s, 9H of $Ti(CH(CMe_3)CH_2CH_2)$], 1.08 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 3.24 [s, 3H of OMe], 3.46 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 3.65 [t, $^3J_{H-H} = 11$, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 3.97 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 4.63 [m, 1H of $Ti(CH(CMe_3)CH_2CH_2)$], 8.30 [s, 1H of $N=CH$]. Selected $^{13}C\{^1H\}$ NMR (C_6D_5Cl , $-20^\circ C$): 6.8 [1C of $Ti(CH(CMe_3)CH_2CH_2)$], 31.1 [3C of $Ti(CH(CMe_3)CH_2CH_2)$], 70.9 [1C of OMe], 99.2 [1C of $Ti(CH(CMe_3)CH_2CH_2)$], 164.6 [1C of $Ti(CH(CMe_3)CH_2CH_2)$], 174.4 [1C of $N=CH$].

Ethylene Trimerization Catalysis with $(FI)Ti(CH_2CMe_3)_2Me$.

(i) A light yellow/orange solution of $(FI)Ti(CH_2CMe_3)_2Me$ (6 mg, 0.009 mmol) in a mixture of C_7D_8 (ca. 0.65 mL) and $o\text{-}C_6H_4F_2$ (ca. 0.05 mL), or C_6D_5Cl (ca. 0.7 mL) was added to an NMR tube equipped with a J. Young valve. The sample was cooled at $-78^\circ C$, and then treated with $B(C_6F_5)_3$ (5 mg, 0.01 mmol) and ethylene (1 atm), resulting in a color change to orange.⁵¹ The sample was continually re-

saturated with ethylene at temperatures $< -20\text{ }^{\circ}\text{C}$ until catalytic activity terminated. The sample was periodically analyzed by ^1H NMR spectroscopy, demonstrating the rapid catalytic production of 1-hexene (by the time the spectra were obtained (ca. 5 minutes after ethylene addition), all of the ethylene was transformed into 1-hexene) and disappearance of $[(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2]^+$. The solution was analyzed by room temperature EPR spectroscopy after catalysis had ceased, indicating the formation of a major Ti^{III} species, with an isotropic g value of 1.958 at room temperature. (ii) In a typical experiment, a solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ (6 mg, 0.009 mmol) in $o\text{-C}_6\text{H}_4\text{F}_2$ (1 mL) was added to a 15 mL ampoule and frozen at $-196\text{ }^{\circ}\text{C}$. The solution was degassed, and allowed to warm to room temperature. The ampoule was then charged with ethylene (1 atm), and then treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (5 mg, 0.01 mmol), and stirred for 20 minutes under constant ethylene pressure (1 atm) at room temperature. After this period, the volume of the solution had increased significantly (ca. 0.3 mL), but only a trace amount of polymer ($< 3\text{ mg}$) had formed. Adamantane was added as an internal integration standard, and the mixture was diluted with benzene, filtered through a plug of silica gel, and analyzed by GC. GC analysis demonstrated the catalytic production of 1-hexene, in addition to C_{10} olefins and C_{14} olefins, with a TON of ca. 2.5×10^3 mmol olefin oligomerized/mmol Ti. (iii) The above procedure was repeated at $-20\text{ }^{\circ}\text{C}$ for 3 hours, giving a TON of ca. 8.9×10^3 mmol olefin oligomerized/mmol Ti.

1-Pentene Trimerization Catalysis with $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$. In a typical experiment, a solution of $(\text{FI})\text{Ti}(\text{CH}_2\text{CMe}_3)_2\text{Me}$ (3 mg, 0.005 mmol) in 1-pentene (1 – 2 mL) was treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (3 mg, 0.006 mmol) at room temperature, and was stirred for ca. 20 minutes to 2 hours. After this period, adamantane 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 demonstrated the formation of C_{15} olefins with a TON of ca. 500 mmol 1-pentene oligomerized/mmol Ti, with no other detectible oligomers. The C_{15} region of the gas chromatogram displayed one major peak ($\sim 85\%$), with two other minor peaks ($\sim 15\%$).

ASSOCIATED CONTENT

Supporting Information

Selected NMR spectra and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

jal@caltech.edu; bercaw@caltech.edu

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Graphical TOC

