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

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S *Supporting Information*

ABSTRACT: Two new precatalysts for ethylene and α-olefin trimerization, $(FI)Ti(CH_2SiMe_3)_2Me$ and $(FI)Ti(CH_2CMe_3)_2Me$ (FI = phenoxy-imine), have been synthesized and structurally characterized by X-ray diffraction. $(FI)Ti(CH_2SiMe_3)_2Me$ can be activated with 1 equiv of $B(C_6F_5)_3$ at room temperature to give the solvent-separated ion pair $[(FI)Ti(CH_2SiMe_3)_2][MeB(C_6F_5)_3]$, which catalytically trimerizes ethylene or 1-pentene to produce 1-hexene or C_{15} olefins, respectively. The neopentyl analogue $(FI)Ti$-$(CH_2CMe_3)_2Me$ is unstable toward activation with $B(C_6F_5)_3$ at room temperature, giving no discernible diamagnetic titanium complexes, but at $-30\ ^\circ C$ the following can be observed by NMR spectroscopy: (i) formation of the bis-neopentyl cation $[(FI)Ti$-$(CH_2CMe_3)_2]^+$, (ii) α-elimination of neopentane to give the neopentylidene complex $[(FI)Ti(=CHCMe_3)]^+$, and (iii) subsequent conversion to the imido-olefin complex $[(MeOAr_2N=)$-$Ti(OArHC=CHCMe_3)]^+$ 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 $[(FI)Ti(CH(CMe_3)CH_2CH_2)]^+$, resulting from addition of ethylene to the neopentylidene $[(FI)Ti(=CHCMe_3)]^+$. None of the complexes observed spectroscopically subsequent to $[(FI)Ti(CH_2CMe_3)_2]^+$ is an intermediate or precursor for ethylene trimerization, but notwithstanding these off-cycle pathways, $[(FI)Ti(CH_2CMe_3)_2]^+$ is a precatalyst that undergoes rapid initiation to generate a catalyst for trimerizing ethylene or 1-pentene.
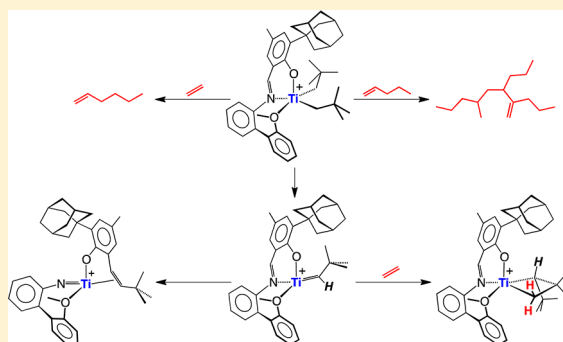
■ INTRODUCTION

The catalytic synthesis of 1-hexene by selective ethylene trimerization, an important industrial process[1] 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 $(FI)TiCl_3$ (FI = (N-(5-methyl-3-(1-adamantyl)salicylidene)-2′-(2″-methoxyphenyl)anilinato) and MAO (10000 equiv); it produces 1-hexene with a turnover number (TON) of $\sim 1.1 \times 10^7$ (mmol of olefin oligomerized)/(mmol of Ti) at 49.3 atm of ethylene.[5] We recently reported that $(FI)TiMe_3$, a putative intermediate upon treatment of $(FI)TiCl_3$ with MAO,[5,6] can be independently synthesized and activated with just 1 equiv of $B(C_6F_5)_3$ to give $[(FI)TiMe_2]$-

$[MeB(C_6F_5)_3]$, an active precatalyst for ethylene trimerization.[7] Furthermore, $(FI)TiMe_3/B(C_6F_5)_3$ 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, $[(FI)TiMe_2][MeB(C_6F_5)_3]$, 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 $[(FI)TiMe_2][MeB(C_6F_5)_3]$, the decomposition product (a Ti^III species), and 1-hexene could be experimentally observed.
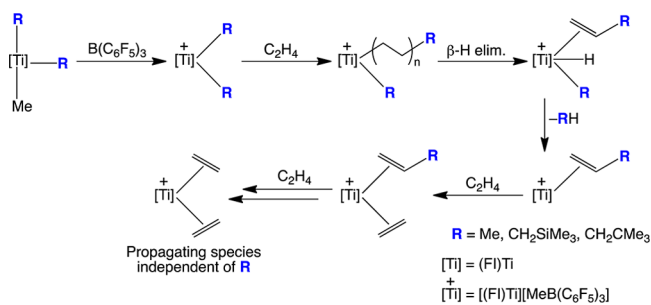
In order to ascertain information about the active catalytic species, we sought a system in which precatalyst initiation is *faster* than trimerization. Previous studies on the propylene polymerization catalysts $[Cp^*CpZrR][MeB(C_6F_5)_3]$ (R = Me, CH_2SiMe_3, CH_2CMe_3) have shown that insertion of propylene into the zirconium–alkyl bond (i.e., catalyst initiation) is

significantly faster for Zr−CH_2CMe_3 in comparison with Zr−Me and Zr−CH_2SiMe_3; the $[Cp^*CpZr(CH_2CMe_3)][MeB-(C_6F_5)_3]$ 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, on the basis of the proposed mechanisms for selective trimerization catalysis (Scheme 1),[5,7,11] the active catalyst should be the same (i.e., $[(FI)Ti^{II}(C_2H_4)_2]^+$), independent of the alkyl ligands in the precatalyst.

Scheme 1

Propagating species independent of R

R = Me, CH_2SiMe_3, CH_2CMe_3

[Ti] = (FI)Ti

[Ti]$^+$ = $[(FI)Ti][MeB(C_6F_5)_3]$

Accordingly, we report here the synthesis of two new potential trimerization precatalysts, $(FI)Ti(CH_2SiMe_3)_2Me$ and $(FI)Ti(CH_2CMe_3)_2Me$, and their behavior upon activation with 1 equiv of $B(C_6F_5)_3$. 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 system based on $(FI)Ti(CH_2CMe_3)_2Me$ does, indeed, undergo faster initiation.

■ RESULTS AND DISCUSSION

Synthesis and Structural Characterization of (FI)Ti Complexes. $(FI)Ti(CH_2SiMe_3)_2Me$ and $(FI)Ti-(CH_2CMe_3)_2Me$ were synthesized by consecutive treatment of a suspension of $(FI)TiCl_3$ in Et_2O with the appropriate Grignard reagents Me_3SiCH_2MgCl or Me_3CCH_2MgCl (2.5 equiv), respectively, and MeMgBr (2.4 equiv) at −30 °C, followed by addition of 1,4-dioxane (Scheme 2).[12] The

Scheme 2
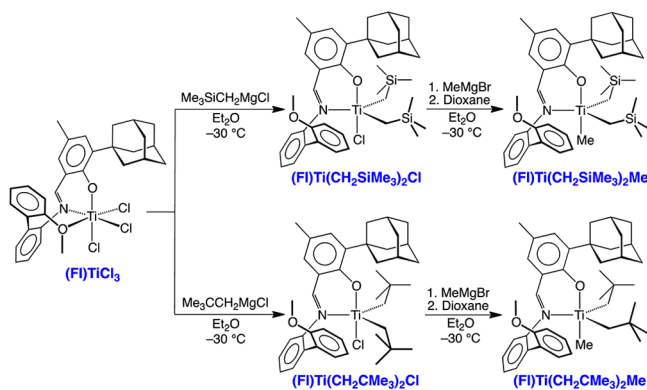
corresponding chlorides, $(FI)Ti(CH_2SiMe_3)_2Cl$ and $(FI)Ti-(CH_2CMe_3)_2Cl$, could be isolated and characterized when the reactions were carried out without MeMgBr addition. All four complexes are soluble in pentane, allowing for easier purification and higher isolated yields in comparison with $(FI)TiMe_3$, 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 toward square pyramidal. The hydrogen atoms of the methylene groups (CH_2XMe_3: 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 $(FI)Ti(CH_2SiMe_3)_2Cl$, $(FI)Ti(CH_2SiMe_3)_2Me$, and $(FI)Ti(CH_2CMe_3)_2Me$ is distal to the methoxy-arene group (C2−Ti−N), whereas the largest angle in $(FI)TiMe_3$ is proximal (N−Ti−C1),[7] suggesting that the sterics of the XMe_3 (X = Si, C) groups have a more significant effect on distorting the geometry toward 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 $(FI)Ti(CH_2CMe_3)_2Cl$ 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).

^1H and ^{13}C NMR spectroscopic studies indicate that all of the complexes are five-coordinate in solution as well, on the basis of the upfield chemical shift of the OMe signal relative to that of $(FI)TiCl_3$.[5] The fluxional nature of the complexes depends on whether the fifth ligand is a chloride or methyl group: at 25 °C $(FI)Ti(CH_2SiMe_3)_2Me$ and $(FI)Ti-(CH_2CMe_3)_2Me$ each display a single ^1H NMR signal for their respective (CH_2XMe_3)$_2$ (X = Si, C) methyl groups, while $(FI)Ti(CH_2SiMe_3)_2Cl$ and $(FI)Ti(CH_2CMe_3)_2Cl$ each display two signals. Furthermore, the chloride complexes display four chemically inequivalent signals for the methylene protons (CH_2XMe_3: 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 leads us to believe that the diamagnetic ring current of the methoxy-arene is a more likely cause.

Activation and Catalysis with $(FI)Ti(CH_2SiMe_3)_2Me$. When a solution of $(FI)Ti(CH_2SiMe_3)_2Me$ in C_6D_6/o-$C_6H_4F_2$ (ca. 0.65 mL/0.05 mL) is treated with 1 equiv of $B(C_6F_5)_3$, selective methide abstraction gives the solvent-separated ion pair $[(FI)Ti(CH_2SiMe_3)_2][MeB(C_6F_5)_3]$ (Scheme 3; [MeB-$(C_6F_5)_3$]$^-$ anion not shown in all schemes). The ion pair has spectroscopic features very similar to those of $[(FI)TiMe_2]$-$[MeB(C_6F_5)_3]$:[7] (i) a downfield OMe chemical shift in comparison with $(FI)Ti(CH_2SiMe_3)_2Me$, indicating coordination to the Ti center,[14] (ii) a $\Delta\delta(m,p$-F) value of 2.5 ppm in the ^{19}F NMR spectrum, suggesting a noncoordinating solvent-separated anion,[15] and (iii) chemically inequivalent and static $SiMe_3$ groups in the ^1H NMR spectrum at 25 °C (δ −0.50 and −0.24 ppm; Figure 2). Furthermore, there are four distinct signals for the methylene protons (CH_2SiMe_3), in accord with a nonfluxional structure (Figure 2).

Upon treatment of the $[(FI)Ti(CH_2SiMe_3)_2][MeB(C_6F_5)_3]$ solution with ethylene (1 atm), 1-hexene is produced rapidly, with slow disappearance of $[(FI)Ti(CH_2SiMe_3)_2]^+$, as determined by ^1H NMR spectroscopy. Hence, as for $[(FI)-TiMe_2][MeB(C_6F_5)_3]$,[7] the rate of trimerization is significantly greater than the rate of initiation. Under a constant pressure of ethylene (1 atm), a solution of $(FI)Ti(CH_2SiMe_3)_2Me/$
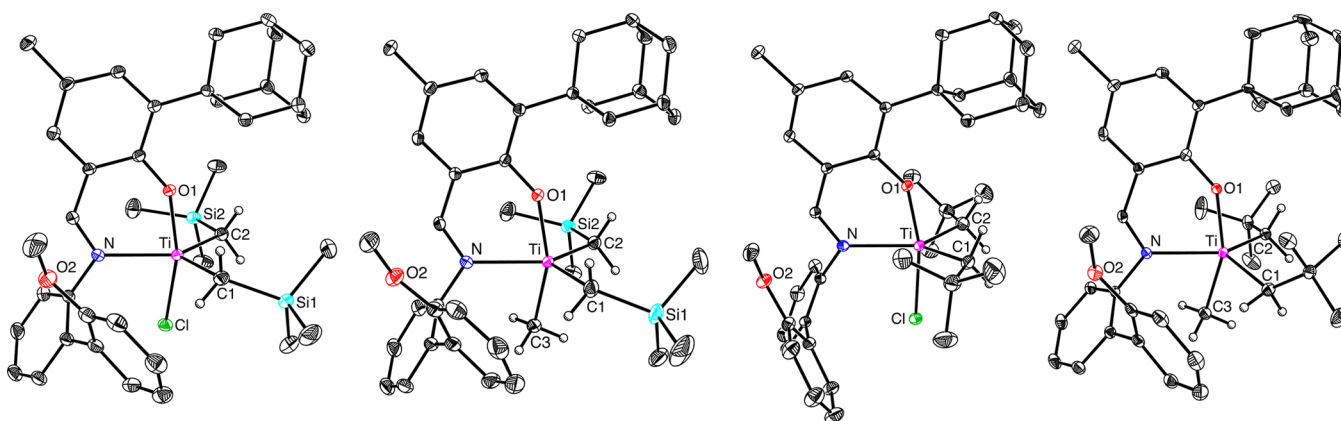
Figure 1. Molecular structures of (FI)Ti(CH$_2$SiMe$_3$)$_2$Cl, (FI)Ti(CH$_2$SiMe$_3$)$_2$Me, (FI)Ti(CH$_2$CMe$_3$)$_2$Cl, and (FI)Ti(CH$_2$CMe$_3$)$_2$Me (left to right). The hydrogen atoms on the FI ligand, CH$_2$SiMe$_3$ methyls, and CH$_2$CMe$_3$ methyls are not shown for clarity.

Table 1. Bond Angles (deg) 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]Δ$_{d-p}$ = (C2−Ti−N) − (N−Ti−C1). [d]The labeling for (FI)TiMe$_3$ is different; the angles (left to right) correspond to N−Ti−C2, C2−Ti−C3, and C3−Ti−N.[7]
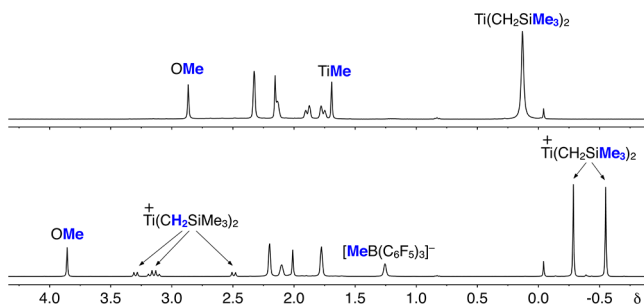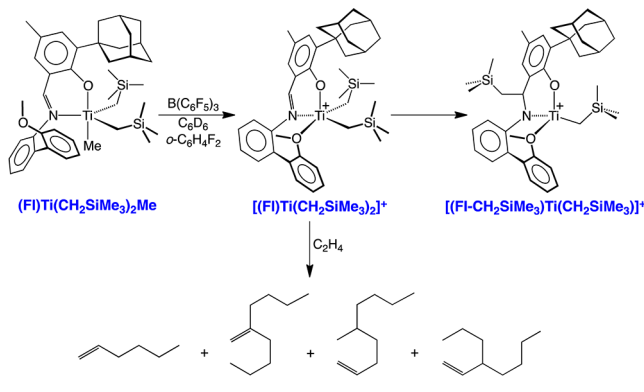
Scheme 3

Figure 2. ^{1}H NMR spectra of (FI)Ti(CH$_2$SiMe$_3$)$_2$Me in C$_6$D$_6$ (top) and of [(FI)Ti(CH$_2$SiMe$_3$)$_2$][MeB(C$_6$F$_5$)$_3$] in C$_6$D$_6$/o-C$_6$H$_4$F$_2$ (bottom) at 25 °C (aromatic region not shown).

B(C$_6$F$_5$)$_3$ (9 μmol, 9 mM) in o-C$_6$H$_4$F$_2$ (1 mL) at 25 °C produces primarily 1-hexene and C$_{10}$ olefins, with only trace amounts of polyethylene formed (<3 mg). The activity (TON of ca. 4.1 × 10^3 (mmol of olefin oligomerized)/(mmol of Ti) after ca. 3 h) is about half that obtained with [(FI)TiMe$_2$]-[MeB(C$_6$F$_5$)$_3$] (Table 2).

Table 2. Ethylene and 1-Pentene Trimerization Catalysis at 25 °C

	ethylene[a]		1-pentene[b]
	TON[c]	TOF[d]	TON[c]
(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]The reaction time is 3 h for a typical run. [b]The reaction time is ca. 12 h for a typical run. [c]TON = (mmol of olefin oligomerized)/(mmol of Ti). [d]TOF = TON/h. [e]Taken from ref 7. [f]The reaction time is 20 min.

(FI)Ti(CH$_2$SiMe$_3$)$_2$Me/B(C$_6$F$_5$)$_3$ also trimerizes α-olefins such as 1-pentene, giving a TON of ca. 900 (Table 2), almost 3 times greater than that for (FI)TiMe$_3$/B(C$_6$F$_5$)$_3$.[7] The higher TON is attributed to the greater solubility of (FI)Ti-(CH$_2$SiMe$_3$)$_2$Me in 1-pentene in comparison with (FI)TiMe$_3$, which forms a suspension with some solid immobilized on the walls of the flask. It is important to note that the selectivity for trimers is greater than 95% and that 85% of the trimers are the same regioisomer (Scheme 4), as observed for (FI)TiMe$_3$/

Scheme 4
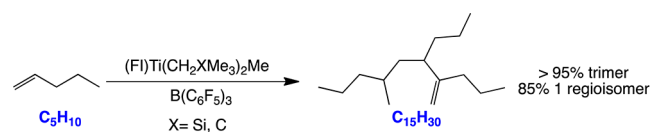
B(C$_6$F$_5$)$_3$,[7] strongly suggesting that (FI)Ti(CH$_2$SiMe$_3$)$_2$Me and (FI)TiMe$_3$ produce the same active catalyst. Likewise, the main decomposition product is the same for both precatalysts: a Ti^{III} species exhibiting a room-temperature EPR signal with an isotropic g value of 1.958.[7] When the ethylene trimerization is monitored 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).

While monitoring catalysis with $[(FI)Ti(CH_2SiMe_3)_2]^+$ in $C_6D_6/o\text{-}C_6H_4F_2$ (ca. 0.65 mL/0.05 mL) by ^{1}H NMR spectroscopy, we observed a new diamagnetic species, which we formulate as $[(FI\text{-}CH_2SiMe_3)Ti(CH_2SiMe_3)]^+$, an isomer of the parent cation $[(FI)Ti(CH_2SiMe_3)_2]^+$ resulting from the migration of one CH_2SiMe_3 group to the imine carbon of the (FI) ligand (Scheme 3).[16] Key new ^{1}H NMR spectroscopic features include (i) a methine signal at δ 4.15 ppm (δ(^{13}C) 79.1 ppm), originating from the imine N=CH, (ii) two signals at δ 0.42 and 0.14 ppm that are diastereotopic methylene protons on the same carbon (δ(^{13}C) 29.7 ppm)[17] and (iii) two SiMe$_3$ signals at δ −0.14 and −0.52 ppm (δ(^{13}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 spectrometry: two major peaks in the electrospray negative ion mode spectrum (m/z 450 and 538) correspond to (FI)$^-$ and (FI-CH$_2$SiMe$_3$)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 $[(FI\text{-}CH_2SiMe_3)\text{-}Ti(CH_2SiMe_3)]^+$ are reduced in situ. This side reaction may account for the lower ethylene trimerization activity for $[(FI)Ti(CH_2SiMe_3)_2]^+$ in comparison with $[(FI)TiMe_2]^+$.[19]

Activation and Catalysis with (FI)Ti(CH$_2$CMe$_3$)$_2$Me. Unlike (FI)TiMe$_3$ and (FI)Ti(CH$_2$SiMe$_3$)$_2$Me, no titanium complex can be detected by ^{1}H NMR spectroscopy from the reaction between (FI)Ti(CH$_2$CMe$_3$)$_2$Me and B(C$_6$F$_5$)$_3$ in $C_6D_6/o\text{-}C_6H_4F_2$ (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 the mixture is allowed to warm to −20 °C in the probe of the NMR spectrometer using a $C_7D_8/o\text{-}C_6H_4F_2$ (ca. 0.65 mL, 0.05 mL) solvent mixture, the ^{1}H, ^{13}C,[17] and ^{19}F NMR spectroscopic features expected for $[(FI)Ti\text{-}(CH_2CMe_3)_2][MeB(C_6F_5)_3]$ can be observed (Scheme 5). As with $[(FI)TiMe_2]^+$ and $[(FI)Ti(CH_2SiMe_3)_2]^+$, they indicate OMe coordination to Ti, chemically inequivalent neopentyl (CH$_2$CMe$_3$) groups, and a noncoordinated solvent-separated anion $[MeB(C_6F_5)_3]^-$.[7] Addition of ethylene (1 atm) at −20
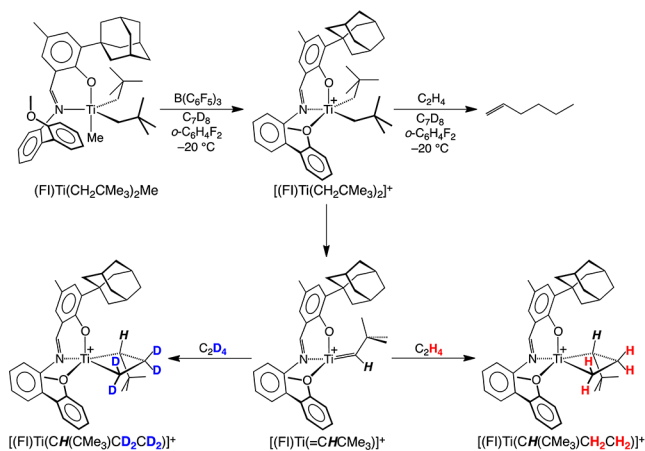
°C to this solution of $[(FI)Ti(CH_2CMe_3)_2]^+$ results in catalytic trimerization with production of 1-hexene (Scheme 5).

The ^{1}H 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$_2$), one methine (CH), and one tert-butyl resonance, on the basis of ^{1}H, COSY, TOCSY, HSQC, and HMBC spectroscopy. These data could be consistent with a Ti^{II}−neoheptene (H$_2$C=CHCH$_2$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 ^{1}H NMR signals seen with C_2H_4, only the methine peak remains with C_2D_4; the neohexene, D$_2$C=CDCH_2CMe$_3$, should show the two methylene signals instead (Scheme 6, top). Instead, we propose

Scheme 6

$\overset{+}{[Ti]} = [(FI)Ti][MeB(C_6F_5)_3]$
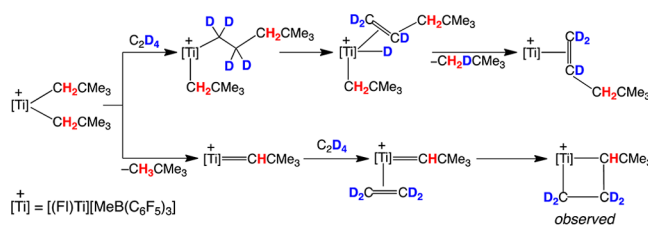
that the new species is the titanacyclobutane $[(FI)Ti(CH\text{-}(CMe_3)CH_2CH_2)]^+$, resulting from $[2 + 2]$ cycloaddition of ethylene with a transient neopentylidene, $[(FI)Ti(=CHCMe_3)]^+$; the isotopologue obtained with ethylene-d_4 would be expected to give the observed single ^{1}H NMR peak (Scheme 6, bottom).[20] A number of titanacyclobutane complexes, typically formed from an alkylidene and olefin, have been reported previously.[21−29]

Analysis by GC/MS[30] of the neopentane generated in the above experiment, carried out under an atmosphere of ethylene-d_4, indicates formation of a ~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 (FI)TiMe$_3$/B(C$_6$F$_5$)$_3$[7] proceeds at a rate comparable with that of competitive α-abstraction (Scheme 6, bottom). Furthermore, (FI)Ti(CH$_2$CMe$_3$)$_2$Me/B(C$_6$F$_5$)$_3$ under an atmosphere of ethylene gives the same major Ti^{III} species (isotropic g value of 1.958) observed for both (FI)TiMe$_3$/B(C$_6$F$_5$)$_3$[7] and (FI)Ti(CH$_2$SiMe$_3$)$_2$Me/B(C$_6$F$_5$)$_3$ (see above). All observations are thus consistent with a common mechanism for initiation.

In an attempt to observe the proposed neopentylidene, we examined the reactivity of $[(FI)Ti(CH_2CMe_3)_2]^+$ at low temperature in the absence of ethylene. Indeed, a solution of $[(FI)Ti(CH_2CMe_3)_2]^+$ in $C_7D_8/o\text{-}C_6H_4F_2$ (ca. 0.65 mL/0.05 mL) at −30 °C is not stable; it converts to the neopentylidene complex $[(FI)Ti(=CHCMe_3)]^+$ by α-elimination of CMe$_4$ over a period of 1 day (Scheme 5). Characteristic NMR spectroscopic features of the Ti=CHCMe$_3$ fragment are ^{1}H and ^{13}C signals at δ 9.91 and 310.9 ppm, respectively, and a $^1J_{C-H}$ coupling constant of 96 Hz,[31] similar to those for other reported titanium alkylidenes.[23,32−36] Addition of C_2H_4 or C_2D_4 (1 atm) at −20 °C to a solution of $[(FI)Ti(=CHCMe_3)]^+$ immediately produces the ^{1}H NMR signals assigned to $[(FI)Ti(CH(CMe_3)CH_2CH_2)]^+$ or $[(FI)Ti(CH\text{-}$

Scheme 5

$(CMe_3)CD_2CD_2)]^+$ (Scheme 5), with complete disappearance of the signals for $[(FI)Ti(=CHCMe_3)]^+$. The ^{13}C NMR chemical shifts (α-C's, 99.2 and 164.5[37] ppm; β-C, 6.8 ppm) are similar to those of other titanacyclobutane complexes, which exhibit upfield β-C signals.[21-28] For example, $Cp_2Ti(CH_2CH(CHMe_2)CH_2)$ has ^{13}C NMR chemical shifts of 75.2 and 13.2 ppm (α and β, respectively).[21]

It is important to note that significantly less 1-hexene is produced when $[(FI)Ti(CH_2CMe_3)_2]^+$ is allowed to convert partially to $[(FI)Ti(=CHCMe_3)]^+$ before addition of ethylene than when ethylene is added immediately after it is generated.[38] This suggests that $[(FI)Ti(=CHCMe_3)]^+$ and $[(FI)Ti(CH(CMe_3)CH_2CH_2)]^+$ are *not* intermediates or precursors for catalytic ethylene trimerization, but rather off-cycle species that lead to decomposition.

To further complicate matters, $[(FI)Ti(=CHCMe_3)]^+$ 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 $[(MeOAr_2N=)Ti(OArHC=CHCMe_3)]^+$ (Scheme 7). ^1H NMR spectroscopic features that support this assign-

Scheme 7

$[(FI)Ti(=CHCMe_3)]^+$ aza-titanacyclobutane $[(MeOAr_2N=)Ti(OArHC=CHCMe_3)]^+$
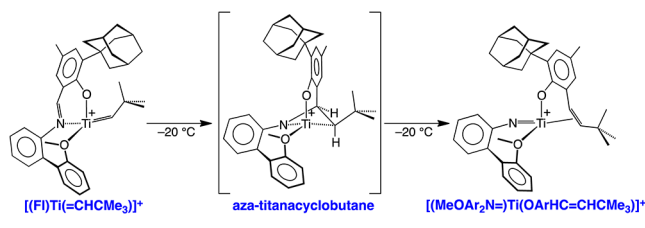
ment are the loss of the FI imine (N=C*H*) signal and the appearance of two olefinic methine CH signals at δ 4.72 and 4.98 ppm, with ^{13}C NMR chemical shifts of 144.5 and 123.3 ppm, respectively. Such a product could form by an intramolecular metathesis reaction between the neopentylidene and imine of the (FI) ligand (Scheme 7); similar transformations have been observed previously by Mindiola and co-workers, employing a $(nacnac)Ti(=CHCMe_3)(OTf)$ 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 $[(MeOAr_2N=)Ti(OArHC=CHCMe_3)]^+$ would be expected to give two organic fragments, $MeOAr_2NH_2$ 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 spectroscopy, respectively, along with GC/MS for both (m/z 199.1 and 324.3). The olefin in $HOArHC=CHCMe_3$ is the Z isomer, on the basis of the characteristically small three-bond coupling constant ($^3J_{H-H} = 12$).[46]

Scheme 8

$[(MeOAr_2N=)Ti(OArHC=CHCMe_3)]^+$ $MeOAr_2NH_2$ $HOArHC=CHCMe_3$
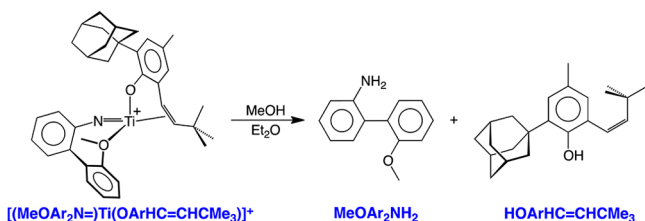
After establishing the above transformations by low temperature NMR spectroscopy, we reexamined the room-temperature reaction of $(FI)Ti(CH_2CMe_3)_2Me$ and $B(C_6F_5)_3$ in $C_6D_6/o\text{-}C_6H_4F_2$. Analysis of the organic material after treatment with MeOH by GC/MS gave the same two major peaks (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 $[(MeOAr_2N=)Ti^{III}(OArHC=CHCMe_3)]$, perhaps with solvent or another L-type ligand coordinated to Ti, although we have no definite evidence on its structure at this time.

Whereas the cation formed from $(FI)Ti(CH_2CMe_3)_2Me$ and $B(C_6F_5)_3$ in C_6D_6 is extremely unstable at room temperature, decomposing in less than 1 min, a solution of the neutral precursor $(FI)Ti(CH_2CMe_3)_2Me$ 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 an 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 values of 199.1 and 324.3. These observations taken together show that $(FI)Ti(CH_2CMe_3)_2Me$ converts to the same Ti^{III} species as does $[(FI)Ti(CH_2CMe_3)_2]^+$, $[(MeOAr_2N=)Ti^{III}(OArHC=CHCMe_3)]$. It thus appears that the Lewis acid $B(C_6F_5)_3$ 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 $(FI)Ti(CH_2CMe_3)_2Me$ and $B(C_6F_5)_3$ still generates a species capable of catalytically trimerizing ethylene and α-olefins. When a solution of $(FI)Ti(CH_2CMe_3)_2Me$ (7 μmol, 7 mM) in $o\text{-}C_6H_4F_2$ (1 mL) is first saturated with ethylene (1 atm) and then treated with 1 equiv of $B(C_6F_5)_3$ 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 $(FI)TiMe_3$ and $(FI)Ti(CH_2SiMe_3)_2Me$, and only trace amounts of polyethylene (<3 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 min (by which time activity had completely ceased), whereas $(FI)Ti(CH_2SiMe_3)_2Me$ and $(FI)TiMe_3$ required 3 h to go to completion. In fact, if the same procedure is repeated at −20 °C for 3 h, a TON of 8.9×10^3 is achieved, which is the highest for this series of precatalysts thus far. The $(FI)Ti(CH_2CMe_3)_2Me/B(C_6F_5)_3$ 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 $[(FI)Ti(CH_2CMe_3)_2]^+$ in comparison with $[(FI)TiMe_2]^+$ and $[(FI)Ti(CH_2SiMe_3)_2]^+$.

The faster rate of initiation is also apparent for α-olefin oligomerization with $(FI)Ti(CH_2CMe_3)_2Me$. When a solution of $(FI)Ti(CH_2CMe_3)_2Me$ in 1-pentene is activated with $B(C_6F_5)_3$, trimerization catalysis proceeds rapidly (Scheme 4) and is complete after only 20 min with a TON of ca. 500. In contrast, when 1-pentene oligomerization with $(FI)Ti(CH_2SiMe_3)_2Me/B(C_6F_5)_3$ is analyzed after 20 min, negligible quantities of trimers are observed. Like $(FI)TiMe_3$ and $(FI)Ti(CH_2SiMe_3)_2Me$, the oligomer selectivity is greater than 95% for trimers, and 85% of the trimers are one

Table 3. Crystal, Intensity Collection, and Refinement Data

	$(FI)Ti(CH_2SiMe_3)_2Cl^a$	$(FI)Ti(CH_2SiMe_3)_2Me^b$	$(FI)Ti(CH_2CMe_3)_2Cl^b$	$(FI)Ti(CH_2CMe_3)_2Me$
lattice	monoclinic	triclinic	triclinic	monoclinic
formula	$C_{43}H_{64}ClNO_3Si_2Ti$	$C_{45}H_{69}NO_2Si_2Ti$	$C_{46}H_{66}ClNO_2Ti$	$C_{42}H_{57}NO_2Ti$
formula wt	782.48	760.09	748.34	655.78
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
$a/\text{Å}$	9.2620(3)	9.6385(5)	12.1256(9)	9.5811(12)
$b/\text{Å}$	22.4163(9)	11.1526(6)	12.3667(10)	20.012(3)
$c/\text{Å}$	21.2155(8)	20.9436(12)	14.8256(11)	19.283(2)
α/deg	90	97.266(3)	92.283(4)	90
β/deg	95.996(2)	97.906(3)	94.294(4)	101.171(4)
γ/deg	90	100.804(3)	106.191(4)	90
$V/\text{Å}^3$	4380.7(3)	2163.4(2)	2124.7(3)	3627.2(8)
Z	4	2	2	4
temp (K)	100(2)	100(2)	100(2)	100(2)
radiation (λ, Å)	0.710 73	0.710 73	0.710 73	0.710 73
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 params	486	487	486	440
R1 ($I > 2\sigma(I)$)	0.0535	0.0469	0.0521	0.0529
wR2 ($I > 2\sigma(I)$)	0.1353	0.1145	0.1329	0.1008
R1 (all data)	0.0756	0.0744	0.0900	0.1128
wR2 (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 Et$_2$O in the asymmetric unit. ^{b}Crystallized with one molecule of pentane in the asymmetric unit.

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, $(FI)Ti(CH_2SiMe_3)_2Me$ and $(FI)Ti(CH_2CMe_3)_2Me$, generate olefin trimerization catalysts upon activation with a stoichiometric amount of $B(C_6F_5)_3$, with selectivities virtually identical with those previously obtained with $(FI)TiMe_3$, strongly suggesting that the active species is the same in the three systems. Whereas trimerization catalysis proceeds at about the same rate with $[(FI)Ti(CH_2SiMe_3)_2]^+$ or $[(FI)-TiMe_2]^+$ as the precatalyst, it is significantly faster for $[(FI)Ti(CH_2CMe_3)_2]^+$, suggesting that the initial goal of accelerating initiation was achieved for the case of neopentyl. For $[(FI)Ti(CH_2CMe_3)_2]^+$ side reactions are rapid as well: it first undergoes α-elimination to the neopentylidene complex $[(FI)Ti(=CHCMe_3)]^+$, which in turn leads to the titanacyclobutane complex $[(FI)Ti(CH(CMe_3)CH_2CH_2)]^+$ or the imido-olefin complex $[(MeOAr_2N=)Ti(OArHC=CHCMe_3)]^+$ in the presence or absence of ethylene, respectively. Unfortunately, none of these species appear to participate in trimerization catalysis; thus, 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, 400, 500, 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$_4$HCl, δ 6.97 for C$_7$D$_7$H).[45] ^{13}C chemical shifts 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, δ 128.87 for C$_7$D$_8$).[49] ^{13}C chemical shifts for all cationic complexes in this report were determined by 2D HSQC and HMBC spectroscopy. Coupling constants are given in Hz. ^{19}F chemical shifts are reported in ppm relative to the absolute ^{1}H chemical shift reference. NMR spectra for $(FI)Ti(CH_2SiMe_3)_2Cl$, $(FI)Ti(CH_2SiMe_3)_2Me$, $(FI)Ti(CH_2CMe_3)_2Cl$, $(FI)Ti(CH_2CMe_3)_2Me$, 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-C$_6$H$_4$F$_2$, and 1-pentene were dried over molecular sieves (3 Å) for at least 2 days and then filtered through activated alumina and stored over molecular sieves (3 Å) prior to use. C$_6$D$_6$, C$_7$D$_8$, and C$_6$D$_5$Cl were dried over molecular sieves (3 Å) for at least 2 days prior to use. Me$_3$SiCH$_2$MgCl and Me$_3$CCH$_2$MgCl were purchased from Aldrich as 1.0 M solutions in Et$_2$O. $(FI)TiCl_3$ was synthesized by our modified[7] literature method.[5]

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data and 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 ref 7 were used. Gas chromatography/mass spectrometry (GC/MS) was performed on an Agilent 6890N instrument using an 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(CH$_2$SiMe$_3$)$_2$Cl. A solution of Me$_3$SiCH$_2$MgCl in Et$_2$O (0.41 mL, 1M, 0.41 mmol) was added to a stirred suspension of (FI)TiCl$_3$ (100 mg, 0.17 mmol) in Et$_2$O (5 mL) cooled to −30 °C, and this mixture was stirred for 5 min 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), and the extract was filtered through Celite and concentrated to ~1 mL, causing crystals to form. The mixture was cooled to −30 °C for several days, thereby depositing yellow crystals which were isolated, washed with cold pentane (−30 °C, ~0.5 mL), and dried in vacuo to give (FI)Ti(CH$_2$SiMe$_3$)$_2$Cl as a yellow crystalline solid (70 mg, 60% yield). X-ray-quality crystals were obtained by cooling a solution of (FI)Ti(CH$_2$SiMe$_3$)$_2$Cl in Et$_2$O/pentane (1/1) to −30 °C. Anal. Calcd for (FI)Ti(CH$_2$SiMe$_3$)$_2$Cl: C, 66.1; H, 7.7; N, 2.0. Found: C, 65.5; H, 7.2; N, 1.8. ^{1}H NMR (C$_6$D$_6$): 0.03 [br s, 9H of Ti(CH$_2$Si*Me*$_3$)$_2$], 0.25 [br s, 1H of Ti(C*H*$_2$SiMe$_3$)$_2$], 0.34 [br s, 9H of Ti(CH$_2$Si*Me*$_3$)$_2$], 1.81 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$], 1.92 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$], 2.17 [s, 3H of C(CH$_2$)$_3$(C*H*)$_3$(CH$_2$)$_3$], 2.17 [s, 3H of ArMe], 2.45 [s, 6H of C(C*H*$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 2.83 [br s, 3H of OMe], 2.99 [br s, 1H of Ti(C*H*$_2$SiMe$_3$)$_2$], 3.15 [br s, 1H of Ti(C*H*$_2$SiMe$_3$)$_2$], 3.74 [br s, 1H of Ti(C*H*$_2$SiMe$_3$)$_2$], 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]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 1.9 [br s, 6C of Ti(CH$_2$Si*Me*$_3$)$_2$], 20.8 [s, 1C of ArMe], 29.5 [s, 3C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 37.3 [s, 3C of C-(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 37.6 [s, 1C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 41.4 [s, 3C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 54.5 [s, 1C of OMe], 102.4 [very br, 2C of Ti(CH$_2$SiMe$_3$)$_2$], 110.3 [s, 1CH of Ar], 121.8 [s, 1C 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(CH$_2$SiMe$_3$)$_2$Me. A solution of Me$_3$SiCH$_2$MgCl in Et$_2$O (0.82 mL, 1 M, 0.82 mmol) was added to a stirred suspension of (FI)TiCl$_3$ (200 mg, 0.33 mmol) in Et$_2$O (7 mL) cooled to −30 °C, the mixture and was stirred for 5 min while warming. The mixture was then cooled to −30 °C and treated with a solution of MeMgBr in Et$_2$O (0.26 mL, 3 M, 0.78 mmol) and was then stirred at 0 °C for 3.5 h. After this period, 1,4-dioxane (~0.1 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), the extract was filtered through a medium-porosity frit with a 0.5 cm bed of Celite, and the filtrate was concentrated to ~2 mL, causing crystals to form. The mixture was cooled to −30 °C for several days, thereby depositing yellow-orange crystals which were isolated, washed with cold pentane (−30 °C, ~1 mL), and dried in vacuo to give (FI)Ti(CH$_2$SiMe$_3$)$_2$Me as a yellow-orange crystalline solid (134 mg, 59% yield). X-ray-quality crystals were obtained by cooling a solution of (FI)Ti(CH$_2$SiMe$_3$)$_2$Me in pentane at −30 °C. Anal. Calcd for (FI)Ti(CH$_2$SiMe$_3$)$_2$Me·0.5C$_5$H$_{12}$: C, 70.5; H, 8.8; N, 1.9. Found: C, 70.7; H, 8.9; N, 1.9. ^{1}H NMR (C$_6$D$_6$): 0.17 [br s, 18H of Ti(CH$_2$Si*Me*$_3$)$_2$], 1.73 [s, 3H of TiMe], 1.81 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$], 1.93 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$], 2.18 [br s, 3H of C-(CH$_2$)$_3$(C*H*)$_3$(CH$_2$)$_3$], 2.20 [s, 3H of ArMe], 2.37 [br s, 6H of C(C*H*$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 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(C*H*$_2$SiMe$_3$)$_2$ not observed. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 2.1 [s, 6C of

Ti(CH$_2$Si*Me*$_3$)$_2$], 20.9 [s, 1C of ArMe], 29.5 [s, 3C of C-(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 37.4 [s, 3C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 37.5 [s, 1C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 41.2 [s, 3C of C-(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 54.6 [s, 1C of OMe], 70.7 [s, 1C of TiMe], 95.4 [very br, 2C of Ti(CH$_2$SiMe$_3$)$_2$], 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(CH$_2$CMe$_3$)$_2$Cl. A solution of Me$_3$CCH$_2$MgCl in Et$_2$O (0.41 mL, 1 M, 0.41 mmol) was added to a stirred suspension of (FI)TiCl$_3$ (100 mg, 0.17 mmol) in Et$_2$O (5 mL) cooled to −30 °C, and the mixture was stirred for 5 min 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), and the extract was filtered through Celite and concentrated to ~1 mL, causing crystals to form. The mixture was cooled to −30 °C for several days, thereby depositing orange crystals which were isolated, washed with cold pentane (−30 °C, ~0.5 mL), and dried in vacuo to give (FI)Ti(CH$_2$CMe$_3$)$_2$Cl as an orange crystalline solid (37 mg, 33% yield). (FI)Ti(CH$_2$CMe$_3$)$_2$Cl is not thermally stable, darkening at room temperature, and should therefore be stored at low temperature (−30 °C for this work). X-ray-quality crystals were obtained by cooling a solution of (FI)Ti(CH$_2$CMe$_3$)$_2$Cl in pentane at −30 °C. Anal. Calcd for (FI)Ti(CH$_2$CMe$_3$)$_2$Cl: C, 72.8; H, 8.1; N, 2.1. Found: C, 71.0; H, 7.8; N, 2.1. ^{1}H NMR (C$_6$D$_6$): 0.98 [br s, 9H of Ti(CH$_2$C*Me*$_3$)$_2$], 1.04 [d, $^2J_{H-H}$ = 10, 1H of Ti(C*H*$_2$CMe$_3$)$_2$], 1.12 [br s, 9H of Ti(CH$_2$C*Me*$_3$)$_2$], 1.81 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$], 1.94 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$], 2.16 [br s, 3H of C(CH$_2$)$_3$(C*H*)$_3$(CH$_2$)$_3$], 2.16 [s, 3H of ArMe], 2.48 [br s, 6H of C(C*H*$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 2.81 [d, $^2J_{H-H}$ = 10, 1H of Ti(C*H*$_2$CMe$_3$)$_2$], 2.90 [s, 3H of OMe], 2.94 [d, $^2J_{H-H}$ = 10, 1H of Ti(C*H*$_2$CMe$_3$)$_2$], 3.29 [d, $^2J_{H-H}$ = 10, 1H of Ti(C*H*$_2$CMe$_3$)$_2$], 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]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 20.8 [s, 1C of ArMe], 29.6 [s, 3C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 33.3 [br s, 6C of Ti(CH$_2$C*Me*$_3$)$_2$], 37.4 [s, 3C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 37.6 [s, 1C of C(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 37.7 [br s, 2C of Ti(CH$_2$CMe$_3$)$_2$], 41.7 [s, 3C of C-(CH$_2$)$_3$(CH)$_3$(CH$_2$)$_3$], 54.6 [s, 1C of OMe], 110.3 [s, 1CH of Ar], 115.6 [very br, 2C of Ti(CH$_2$CMe$_3$)$_2$], 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(CH$_2$CMe$_3$)$_2$Me. A solution of Me$_3$CCH$_2$MgCl in Et$_2$O (0.82 mL, 1 M, 0.82 mmol) was added to a stirred suspension of (FI)TiCl$_3$ (200 mg, 0.33 mmol) in Et$_2$O (7 mL) cooled to −30 °C, and the mixture was stirred for 5 min while warming. The mixture was then cooled to −30 °C and treated with a solution of MeMgBr in Et$_2$O (0.26 mL, 3 M, 0.78 mmol) and was then stirred at 0 °C for 3.5 h. After this period, 1,4-dioxane (~0.1 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), the extract was filtered through a medium-porosity frit with a 0.5 cm bed of Celite, and the filtrate was concentrated to ~2 mL, causing crystals to form. The mixture was cooled to −30 °C for several days, thereby depositing orange crystals which were isolated, washed with cold pentane (−30 °C, ~1 mL), and dried in vacuo to give (FI)Ti-(CH$_2$CMe$_3$)$_2$Me as an orange crystalline solid (96 mg, 44% yield).

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dx.doi.org/10.1021/ja5055687 | *J. Am. Chem. Soc.* 2014, 136, 10790−10800

(FI)Ti(CH$_2$CMe$_3$)$_2$Me is not thermally stable in the solid state or solution, darkening at room temperature, and should therefore be stored at low temperature (-30 °C for this work). Solutions of (FI)Ti(CH$_2$CMe$_3$)$_2$Me in C$_6$D$_6$ 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 (FI)Ti(CH$_2$CMe$_3$)$_2$Me in pentane at -30 °C. ^{1}H NMR (C$_6$D$_6$): 1.07 [br s, 18H of Ti(CH$_2$CMe_3)$_2$], 1.78 [s, 3H of TiMe], 1.81 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH$_3$)(CH_2)$_3$], 1.94 [d, AB pattern, $^2J_{H-H}$ = 12, 3H of C(CH$_2$)$_3$(CH$_3$)(CH_2)$_3$], 2.16 [br s, 3H of C(CH$_2$)$_3$(CH_3)(CH$_2$)$_3$], 2.20 [s, 3H of ArMe], 2.39 [br s, 6H of C(CH_2)$_3$(CH$_3$)(CH$_2$)$_3$], 2.93 [s, 3H of OMe], 6.25 [d, $^3J_{H-H}$ = 8, 1H of Ar], 6.78 [d, $^4J_{H-H}$ = 2, 1H of Ar], 6.82 [br t, $^3J_{H-H}$ = 7, 1H of Ar], 6.93 [m, 1H of Ar], 7.02 [dd, $^3J_{H-H}$ = 8, $^4J_{H-H}$ = 1, 1H of Ar], 7.09 [dt, $^4J_{H-H}$ = 1, $^3J_{H-H}$ = 8, 1H of Ar], 7.16 [m, 1H of Ar], 7.21 [br d, $^3J_{H-H}$ = 7, 1H of Ar], 7.27 [br d, $^3J_{H-H}$ = 7, 1H of Ar], 7.32 [d, $^4J_{H-H}$ = 2, 1H of Ar], 8.62 [s, 1H of N=CH], 4H of Ti(CH_2CMe$_3$)$_2$ not observed. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 20.8 [s, 1C of ArMe], 29.5 [s, 3C of C(CH$_2$)$_3$(CH$_3$)(CH$_2$)$_3$], 33.7 [s, 6C of Ti(CH$_2$CMe_3)$_2$], 37.4 [s, 2C of Ti(CH$_2$CMe_3)$_2$], 37.4 [s, 1C of C(CH$_2$)$_3$(CH$_3$)(CH$_2$)$_3$], 37.5 [s, 3C of C(CH$_2$)$_3$(CH$_3$)(CH$_2$)$_3$], 41.4 [s, 3C of C(CH$_2$)$_3$(CH$_3$)(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 Ti(CH$_2$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 N=CH].

Reaction between (FI)Ti(CH$_2$SiMe$_3$)$_2$Me and B(C$_6$F$_5$)$_3$. A light yellow solution of (FI)Ti(CH$_2$SiMe$_3$)$_2$Me (6 mg, 0.009 mmol) in a mixture of C$_6$D$_6$ (ca. 0.65 mL) and o-C$_6$H$_4$F$_2$ (ca. 0.05 mL) in an NMR tube equipped with a J. Young valve was treated with B(C$_6$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 ^{1}H, ^{19}F, COSY, HSQC, and HMBC NMR spectroscopy, thereby demonstrating conversion to [(FI)Ti(CH$_2$SiMe$_3$)$_2$][MeB(C$_6$F$_5$)$_3$] (ca. 80% by ^{1}H NMR integration). ^{1}H NMR (C$_6$D$_6$/o-C$_6$H$_4$F$_2$): -0.50 [s, 9H of Ti(CH$_2$SiMe_3)$_2$], -0.24 [s, 9H of Ti(CH$_2$SiMe_3)$_2$], 1.29 [br s, 3H of MeB(C$_6$F$_5$)$_3$], 1.82 [br s, 6H of C(CH$_2$)$_3$(CH$_3$)(CH_2)$_3$], 2.05 [s, 3H of ArMe], 2.14 [s, 3H of C(CH$_2$)$_3$(CH_3)(CH$_2$)$_3$], 2.24 [s, 6H of C(CH_2)$_3$(CH$_3$)(CH$_2$)$_3$], 2.52 [d, $^2J_{H-H}$ = 11, 1H of Ti(CH_2SiMe$_3$)$_2$], 3.18 [AB quartet, $^2J_{H-H}$ = 11, 2H of Ti(CH_2SiMe$_3$)$_2$], 3.34 [d, $^2J_{H-H}$ = 11, 1H of Ti(CH_2SiMe$_3$)$_2$], 3.89 [s, 3H of OMe], 6.30 [d, $^3J_{H-H}$ = 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, $^3J_{H-H}$ = 8, 1H of Ar], 7.34 [s, 1H of Ar], 7.77 [s, 1H of N=CH]. Selected ^{13}C{^{1}H} NMR (C$_6$D$_6$/o-C$_6$H$_4$F$_2$): 1.3 [3C of Ti(CH$_2$SiMe_3)$_2$], 1.4 [3C of Ti(CH$_2$SiMe_3)$_2$], 11.3 [1C of MeB(C$_6$F$_5$)$_3$], 20.2 [1C of ArMe], 29.0 [3C of C(CH$_2$)$_3$(CH$_3$)(CH$_2$)$_3$], 36.8 [3C of C(CH$_2$)$_3$(CH$_3$)(CH$_2$)$_3$], 41.8 [3C of C(CH$_2$)$_3$(CH$_3$)(CH$_2$)$_3$], 72.1 [1C of OMe], 109.2 [1C of Ti(CH$_2$SiMe$_3$)$_2$], 110.7 [1C of Ti(CH$_2$SiMe$_3$)$_2$], 174.5 [1C of N=CH]. ^{19}F NMR (C$_6$D$_6$/o-C$_6$H$_4$F$_2$): -166.9 [t, $^3J_{F-F}$ = 20, 6F of MeB(C$_6$F$_5$)$_3$, para-F], -164.4 [t, $^3J_{F-F}$ = 21, 3F of MeB(C$_6$F$_5$)$_3$, meta-F], -131.7 [d, $^3J_{F-F}$ = 21, 6F of MeB(C$_6$F$_5$)$_3$, ortho-F].

The solution described above was monitored over time, demonstrating conversion to [(FI-CH$_2$SiMe$_3$)Ti(CH$_2$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 values consistent with (FI)H and (FI-CH$_2$SiMe$_3$)H$_2$. Selected ^{1}H NMR (C$_6$D$_6$/o-C$_6$H$_4$F$_2$): -0.52 [s, 9H of (FI-CH$_2$SiMe_3)], -0.14 [s, 9H of Ti(CH$_2$SiMe_3)], 0.13 [dd, $^2J_{H-H}$ = 14, $^3J_{H-H}$ = 4, 1H of (N-ArCH-CH_2SiMe$_3$)], 0.42 [dd, $^2J_{H-H}$ = 14, $^3J_{H-H}$ = 10, 1H of (N-ArCH-CH_2SiMe$_3$)], 2.36 [d, $^2J_{H-H}$ = 10, 1H of Ti(CH_2SiMe$_3$)], 2.66 [d, $^2J_{H-H}$ = 10, 1H of Ti(CH_2SiMe$_3$)], 3.45 [s, 3H of OMe], 4.15 [dd, $^3J_{H-H}$ = 11, $^3J_{H-H}$ = 4, 1H of (N-ArCH-CH$_2$SiMe$_3$)]. Selected ^{13}C{^{1}H} NMR (C$_6$D$_6$/o-C$_6$H$_4$F$_2$): -1.9 [3C of (FI-CH$_2$SiMe_3)], 1.7 [3C of Ti(CH$_2$SiMe_3)], 29.7 [1C of (N-ArCH-CH_2SiMe$_3$)], 70.5 [1C

of OMe], 79.1 [1C of (N-ArCH-CH$_2$SiMe$_3$)], 105.7 [1C of Ti(CH$_2$SiMe$_3$)].

Ethylene Trimerization Catalysis with (FI)Ti(CH$_2$SiMe$_3$)$_2$Me. (i) A solution of (FI)Ti(CH$_2$SiMe$_3$)$_2$Me (6 mg, 0.009 mmol) in a mixture of C$_6$D$_6$ (ca. 0.65 mL) and o-C$_6$H$_4$F$_2$ (ca. 0.05 mL) in an NMR tube equipped with a J. Young valve was treated with B(C$_6$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 ^{1}H NMR spectroscopy, thereby demonstrating conversion to [(FI)Ti(CH$_2$SiMe$_3$)$_2$][MeB(C$_6$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 resaturated with ethylene until catalytic activity terminated. The sample was periodically analyzed by ^{1}H NMR spectroscopy, demonstrating the catalytic production of 1-hexene and slow disappearance of [(FI)Ti(CH$_2$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 in intensity over the time course of the reaction.

(ii) In a typical experiment, a solution of (FI)Ti(CH$_2$SiMe$_3$)$_2$Me (6 mg, 0.009 mmol) in o-C$_6$H$_4$F$_2$ (1 mL) in a 15 mL ampule was treated with B(C$_6$F$_5$)$_3$ (5 mg, 0.01 mmol) at room temperature. The solution was frozen, degassed, and allowed to warm to room temperature. The ampule was then charged with ethylene (1 atm) and stirred for ca. 3 h 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 of olefin oligomerized)/(mmol of Ti).

1-Pentene Trimerization Catalysis with (FI)Ti(CH$_2$SiMe$_3$)$_2$Me. (i) In a typical experiment, a solution of (FI)Ti(CH$_2$SiMe$_3$)$_2$Me (3 mg, 0.004 mmol) in 1-pentene (1−2 mL) was treated with B(C$_6$F$_5$)$_3$ (2 mg, 0.004 mmol) at room temperature and was stirred for ca. 12 h. 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 of 1-pentene oligomerized)/(mmol of 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%).

(ii) When the above procedure was repeated with only 20 min stirring, GC analysis demonstrated negligible C$_{15}$ production.

Reaction between (FI)Ti(CH$_2$CMe$_3$)$_2$Me and B(C$_6$F$_5$)$_3$. (i) A light yellow-orange solution of (FI)Ti(CH$_2$CMe$_3$)$_2$Me (6 mg, 0.009 mmol) in a mixture of C$_6$D$_6$ (ca. 0.65 mL) and o-C$_6$H$_4$F$_2$ (ca. 0.05 mL) in an NMR tube equipped with a J. Young valve was treated with B(C$_6$F$_5$)$_3$ (5 mg, 0.01 mmol) at room temperature, resulting in an immediate color change to orange. After ca. 1 min, the solution turned dark brown and analysis by ^{1}H NMR spectroscopy gave no indication of any diamagnetic (FI)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 values of 199.1 and 324.3.

(ii) A light yellow-orange solution of (FI)Ti(CH$_2$CMe$_3$)$_2$Me (6 mg, 0.009 mmol) in a mixture of C$_7$D$_8$ (ca. 0.65 mL) and o-C$_6$H$_4$F$_2$ (ca. 0.05 mL) or C$_6$D$_5$Cl (ca. 0.7 mL) was placed in an NMR tube equipped with a J. Young valve. The sample was cooled to -78 °C and then treated with B(C$_6$F$_5$)$_3$ (5 mg, 0.01 mmol), resulting in a color change to orange.[41] The sample was allowed to warm to either -30 or -20 °C in the probe of the NMR spectrometer and was analyzed by ^{1}H, ^{19}F, COSY, HSQC and HMBC NMR spectroscopy, thereby demonstrating conversion to [(FI)Ti(CH$_2$CMe$_3$)$_2$][MeB(C$_6$F$_5$)$_3$] (ca. 80% by ^{1}H NMR integration). ^{1}H NMR (C$_6$D$_5$Cl, -20 °C): 0.68 [s, 9H of Ti(CH$_2$CMe_3)$_2$], 0.80 [s, 9H of Ti(CH$_2$CMe_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{^{1}H} NMR (C_6D_5Cl, −20 °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 ^{1}H NMR (C_7D_8/o-$C_6H_4F_2$, −20 °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{^{1}H} NMR (C_7D_8/o-$C_6H_4F_2$, −20 °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-$C_6H_4F_2$, −30 °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$_2$N═)Ti(OArHC═CHCMe$_3$)]$^+$. A light yellow-orange solution of (FI)Ti(CH_2CMe_3)$_2$Me (6 mg, 0.009 mmol) in a mixture of C_7D_8 (ca. 0.65 mL) and o-$C_6H_4F_2$ (ca. 0.05 mL) or C_6D_5Cl (ca. 0.7 mL) was placed in a small vial and cooled to −30 °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 °C for ca. 1 day. The solution was then pipetted into an NMR tube equipped with a J. Young valve (which was precooled to < −78 °C), sealed, and then cooled to −78 °C. The sample was allowed to warm to −20 °C in the probe of the NMR spectrometer and was analyzed by ^{1}H, COSY, HSQC, and HMBC NMR spectroscopy, thereby demonstrating formation of [(FI)Ti(═CHCMe$_3$)]$^+$. Selected ^{1}H NMR (C_7D_8/o-$C_6H_4F_2$, −20 °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{^{1}H} NMR (C_7D_8/o-$C_6H_4F_2$, −20 °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 ^{1}H NMR (C_6D_5Cl, −20 °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{^{1}H} NMR (C_6D_5Cl, −20 °C): 312.3 [1C of Ti(═CHCMe$_3$)].

At −20 °C, [(FI)Ti(═CHCMe$_3$)]$^+$ converted to [(MeOAr$_2$N═)-Ti(OArHC═CHCMe$_3$)]$^+$ over a period of hours, and this compound was analyzed by ^{1}H, COSY, HSQC, and HMBC NMR spectroscopy. Selected ^{1}H NMR (C_7D_8/o-$C_6H_4F_2$, −20 °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{^{1}H} NMR (C_7D_8/o-$C_6H_4F_2$, −20 °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)$_2$Me (40 mg, 0.061 mmol) in Et$_2$O (ca. 3 mL) was placed in a large vial and cooled to −30 °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 °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). ^{1}H 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{^{1}H} 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$_2$CH$_2$)]$^+$. A light yellow-orange solution of (FI)Ti(CH_2CMe_3)$_2$Me (6 mg, 0.009 mmol) in a mixture of C_7D_8 (ca. 0.65 mL) and o-$C_6H_4F_2$ (ca. 0.05 mL) or C_6D_5Cl (ca. 0.7 mL) was placed in an NMR tube equipped with a J. Young valve. The sample was cooled to −78 °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 or −20 °C in the probe of the NMR spectrometer and was analyzed by ^{1}H, COSY, TOCSY, HSQC, and HMBC NMR spectroscopy, thereby demonstrating the catalytic production of 1-hexene and the formation of [(FI)Ti(CH(CMe$_3$)CH$_2$CH$_2$)]$^+$. An analogous experiment was conducted with ethylene-d_4, demonstrating formation of [(FI)Ti(CH-(CMe$_3$)CD$_2$CD$_2$)]$^+$. Selected ^{1}H NMR (C_7D_8/o-$C_6H_4F_2$, −20 °C): 0.67 [s, 9H of Ti(CH(CMe_3)CH$_2$CH$_2$)], 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$_2$CH$_2$)], 3.82 [m, 1H of Ti(CH(CMe$_3$)CH$_2$CH_2)], 4.56 [m, 1H of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 7.79 [s, 1H of N═CH]. Selected ^{13}C{^{1}H} NMR (C_7D_8/o-$C_6H_4F_2$, −20 °C): 6.8 [1C of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 30.9 [3C of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 70.7 [1C of OMe], 99.2 [1C of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 164.5 [1C of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 174.4 [1C of N═CH]. Selected ^{1}H NMR (C_6D_5Cl, −20 °C): 0.72 [s, 9H of Ti(CH(CMe_3)CH$_2$CH$_2$)], 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$_2$CH$_2$)], 3.65 [t, $^3J_{H-H}$ = 11, 1H of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 3.97 [m, 1H of Ti(CH(CMe$_3$)CH$_2$CH_2)], 4.63 [m, 1H of Ti(CH(CMe$_3$)CH$_2$CH_2)], 8.30 [s, 1H of N═CH]. Selected ^{13}C{^{1}H} NMR (C_6D_5Cl, −20 °C): 6.8 [1C of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 31.1 [3C of Ti(CH(CMe_3)CH$_2$CH$_2$)], 70.9 [1C of OMe], 99.2 [1C of Ti(CH(CMe$_3$)CH$_2$CH$_2$)], 164.6 [1C of Ti(CH(CMe$_3$)-CH$_2$CH$_2$)], 174.4 [1C of N═CH].

Ethylene Trimerization Catalysis with (FI)Ti(CH$_2$CMe$_3$)$_2$Me. (i) A light yellow-orange solution of (FI)Ti(CH$_2$CMe$_3$)$_2$Me (6 mg, 0.009 mmol) in a mixture of C_7D_8 (ca. 0.65 mL) and o-$C_6H_4F_2$ (ca. 0.05 mL) or C_6D_5Cl (ca. 0.7 mL) was placed in an NMR tube equipped with a J. Young valve. The sample was cooled to −78 °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 resaturated with ethylene at temperatures <−20 °C until catalytic activity terminated. The sample was periodically analyzed by ^{1}H NMR spectroscopy, demonstrating the rapid catalytic production of 1-hexene (by the time the spectra were obtained (ca. 5 min after ethylene addition), all of the ethylene was transformed into 1-hexene) and disappearance of [(FI)Ti(CH$_2$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 (FI)Ti(CH$_2$CMe$_3$)$_2$Me (6 mg, 0.009 mmol) in o-$C_6H_4F_2$ (1 mL) was placed in a 15 mL ampule and frozen at −196 °C. The solution was degassed and warmed to room temperature. The ampule was then charged with ethylene (1 atm), treated with B(C_6F_5)$_3$ (5 mg, 0.01 mmol), and stirred for 20 min 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 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 of olefin oligomerized)/(mmol of Ti).

(iii) The above procedure was repeated at −20 °C for 3 h, giving a TON of ca. 8.9×10^3 (mmol of olefin oligomerized)/(mmol of Ti).

1-Pentene Trimerization Catalysis with (FI)Ti(CH₂CMe₃)₂Me.

1-Pentene Trimerization Catalysis with $(FI)Ti(CH_2CMe_3)_2Me$. In a typical experiment, a solution of $(FI)Ti(CH_2CMe_3)_2Me$ (3 mg, 0.005 mmol) in 1-pentene (1−2 mL) was treated with $B(C_6F_5)_3$ (3 mg, 0.006 mmol) at room temperature and was stirred for ca. 20 min to 2 h. 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 of 1-pentene oligomerized)/(mmol of 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%).

ASSOCIATED CONTENT

ⓢ Supporting Information
Figures giving selected NMR spectra and CIF files giving crystallographic data for $(FI)Ti(CH_2SiMe_3)_2Cl$, $(FI)Ti(CH_2SiMe_3)_2Me$, $(FI)Ti(CH_2CMe_3)_2Cl$ and $(FI)Ti(CH_2CMe_3)_2Me$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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(38) It is difficult to achieve complete conversion to [(FI)Ti(═CHCMe$_3$)]$^+$ because it is also not stable in solution; the small remaining quantities of [(FI)Ti(CH$_2$CMe$_3$)$_2$]$^+$ appear to be responsible for the 1-hexene production, which is 3 times less than when [(FI)Ti(CH$_2$CMe$_3$)$_2$]$^+$ is treated with ethylene under similar conditions. When [(FI)Ti(CH$_2$CMe$_3$)$_2$]$^+$ is allowed to convert fully to a mixture of [(FI)Ti(═CHCMe$_3$)]$^+$ and [(MeOAr$_2$N═)Ti(OArHC═CHCMe$_3$)]$^+$ before adding ethylene, negligible quantities of 1-hexene are produced.

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