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

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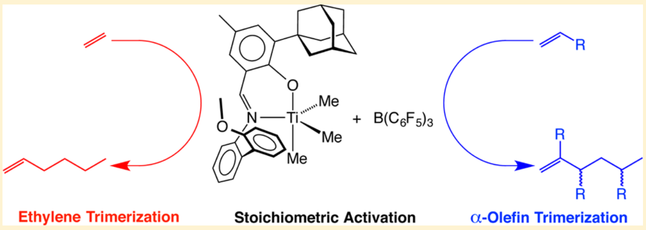
Supporting Information

ABSTRACT: Reaction of a trimethyl titanium complex, (FI)$TiMe_3$ (FI = phenoxy-imine), with 1 equiv of $B(C_6F_5)_3$ gives [(FI)$TiMe_2$][$MeB(C_6F_5)_3$], an effective precatalyst for the selective trimerization of ethylene. Mechanistic studies indicate that catalyst initiation involves generation of an active Ti^{II} species by olefin insertion into a Ti−Me bond, followed by β-H elimination and reductive elimination of methane, and that initiation is slow relative to trimerization. (FI)$TiMe_3$/$B(C_6F_5)_3$ also leads to a competent catalyst for the oligomerization of α-olefins, displaying high selectivity for trimers (>95%), approximately 85% of which are one regioisomer. This catalyst system thus shows promise for selectively converting light α-olefins into transportation fuels and lubricants.



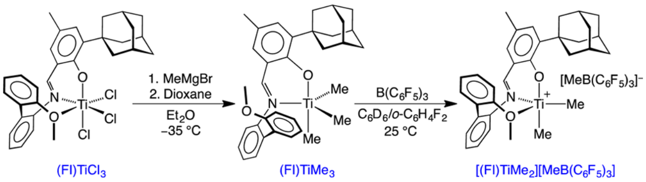
The selective trimerization of ethylene to 1-hexene,[1,2] a comonomer for production of linear low-density polyethylene (LLDPE), has been extensively studied[3] and is an important industrial process.[4] Most research in this area has involved ill-defined catalyst systems, requiring large excesses (typically 1000-fold or more) of an activator such as MAO.[5] Stoichiometric activation of catalysts is rare.[6,7] Hence, many mechanistic aspects are at best poorly understood, in contrast to the well-studied field of ethylene polymerization, where stoichiometrically activated catalysts are common.[8]

While ethylene trimerization catalysis is well precedented, research concerning the oligomerization of linear α-olefins (LAOs) is scarce.[9−14] In fact, to the best of our knowledge, the only effective catalyst for selective LAO trimerization is (R_3TAC)$CrCl_3$ (R_3TAC = trialkyltriazacyclohexane), which converts 1-decene and 1-dodecene to C_{30} and C_{36} olefins, respectively;[9] it should be emphasized that this system also requires activation by excess MAO (100 equiv). Light LAOs are significant components of crude oil as well as being produced in refinery processes such as fluidized catalytic cracking, but (aside from the aforementioned production of LLDPE) are not widely used; upgrading light LAOs to heavier olefins by oligomerization could be a valuable route to higher value products, such as diesel and/or jet fuel,[15] lubricants,[16] and precursors to surfactants and detergents. For example, trimerization of 1-pentene or 1-hexene would lead to C_{15} and C_{18} hydrocarbons, components of jet/diesel fuel. Trimerization of 1-decene is currently used industrially for the production of synthetic lubricants (e.g., Mobil 1),[16] but these processes give distributions of oligomers;[17] selective trimerization is most desirable, as it eliminates the need for additional energy-intensive separations.

In 2010, Fujita et al. reported a new, highly active, and selective ethylene trimerization system (~92% selective for 1-hexene, turnover number (TON) ~1.1 × 10^7 (mmol of olefin oligomerized)/(mmol of Ti) at 49.3 atm) based on (FI)$TiCl_3$ (FI = *N*-(5-methyl-3-(1-adamantyl)salicylidene)-2′-(2″-methoxyphenyl)anilinato) as the precatalyst; as in most other systems, a large excess (10000 equiv in this case) of MAO is required for activation.[18,19] In order to gain mechanistic insight into this catalytic system, we sought to develop a precatalyst that could be activated stoichiometrically. We report here the synthesis and structural characterization of (FI)$TiMe_3$, which can selectively trimerize ethylene upon activation with 1 equiv of $B(C_6F_5)_3$. Moreover, (FI)$TiMe_3$/$B(C_6F_5)_3$ can oligomerize LAOs with remarkable selectivity (>95%) for trimers, ~85% of which consist of a single regioisomer.

Treatment of a suspension of (FI)$TiCl_3$ in Et_2O at −35 °C with MeMgBr, followed by addition of 1,4-dioxane, afforded yellow (FI)$TiMe_3$ (Scheme 1).[20] Single-crystal X-ray diffraction studies established the five-coordinate, pseudo-trigonal-bipyramidal geometry shown in Figure 1.[21] The upfield ^{1}H NMR chemical shift for the methoxy group (δ 2.93 ppm, Figure 2) relative to that of (FI)$TiCl_3$ (δ 4.09 ppm), which is six-coordinate in the solid state,[18] indicates that (FI)$TiMe_3$ is also

Scheme 1



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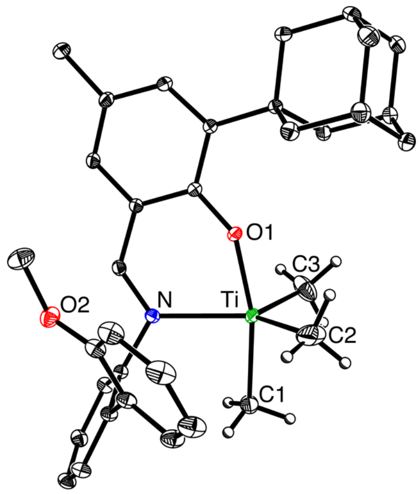


Figure 1. Molecular structure of (FI)TiMe$_3$. H atoms on the FI ligand are not shown for clarity.

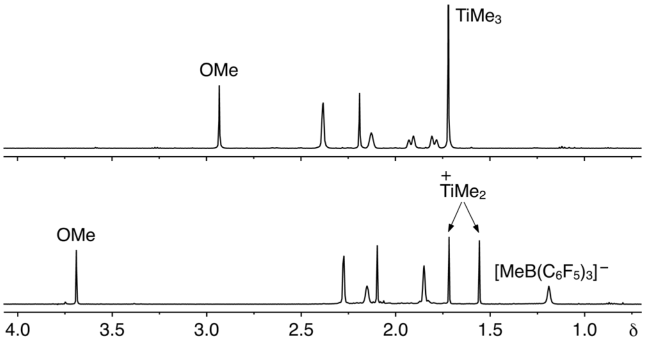


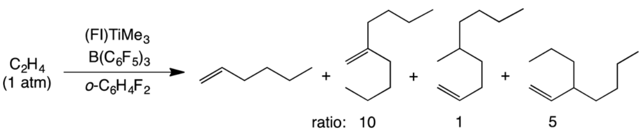
Figure 2. ^{1}H NMR spectra of (top) (FI)TiMe$_3$ in C_6D_6 and (bottom) [(FI)TiMe$_2$][MeB(C_6F_5)$_3$] in C_6D_6/*o*-$C_6H_4F_2$ at 25 °C. The aromatic region is not shown.

five-coordinate in solution (C_6D_6). Furthermore, the three methyl groups of the TiMe$_3$ fragment show a single ^{1}H NMR signal from 25 to −80 °C (Figure 2), indicating the fluxional nature of (FI)TiMe$_3$.

Treatment of a solution of (FI)TiMe$_3$ in C_6D_6/*o*-$C_6H_4F_2$ (ca. 0.6 mL/0.1 mL) with 1 equiv of B(C_6F_5)$_3$ at 25 °C immediately generates a new species, characterized by NMR spectroscopy (Figure 2) as [(FI)TiMe$_2$][MeB(C_6F_5)$_3$] (Scheme 1), in approximately 80% yield. The downfield chemical shift of the OMe group (δ 3.69 ppm, Figure 2) in comparison to the signal for (FI)TiMe$_3$ indicates coordination to Ti, while the ^{1}H NMR chemical shift of [MeB(C_6F_5)$_3$]$^-$ (δ 1.19 ppm, Figure 2) and the $\Delta\delta$(*m*,*p*-F) value of 2.5 ppm in the ^{19}F NMR spectrum are consistent with a noncoordinating solvent-separated anion, rather than a coordinating tight ion pair.[22] Interestingly, although five-coordinate complexes are typically fluxional[23] on the NMR time scale (e.g. (FI)TiMe$_3$), the two methyl groups of [(FI)TiMe$_2$] are chemically inequivalent and static in the ^{1}H NMR spectrum at 25 °C (δ 1.56 and 1.72 ppm, Figure 2); however, a slow exchange process can be observed by exchange spectroscopy (EXSY). We suggest that the tridentate FI ligand inhibits Berry pseudorotation;[24] loose coordination of a solvent molecule may also be involved.

[(FI)TiMe$_2$][MeB(C_6F_5)$_3$] is an effective precatalyst for ethylene trimerization.[25] Exposure of a solution of (FI)TiMe$_3$/B(C_6F_5)$_3$ (7 μmol, 7 mM) in *o*-$C_6H_4F_2$ (1 mL) to 1 atm of ethylene at 25 °C produces primarily 1-hexene and C_{10} olefins; small amounts of C_{14} olefins (~5%) are also observed, with only trace amounts of polyethylene (<3 mg) formed. The C_{10} and C_{14} olefins arise from cotrimerization of ethylene with 1-hexene and C_{10} respectively; the relative amounts depend upon catalyst concentration and the degree of conversion to which the reaction is carried out. Overall selectivity for olefin trimers is greater than 99%, with a turnover frequency (TOF) of ca. 2.7 × 10^3 (mmol of olefin oligomerized)/((mmol of Ti) h); a total of ca. 8.3 × 10^3 turnovers were achieved after 3 h. The activity of the original (FI)TiCl$_3$/MAO system can be extrapolated (from the high-pressure data and second-order dependence on ethylene pressure reported[18]) to a TOF value of 4.6 × 10^3 at 1 atm, which is similar to our experimental value for (FI)TiMe$_3$/B(C_6F_5)$_3$. Three major C_{10} olefins are produced, one 2-substituted α-olefin and two α-olefins (Scheme 2).[20] In order to ascertain the relative rate of LAO and ethylene incorporation, a competition experiment between 1-heptene and ethylene (20/1 mole ratio) was carried out. At low conversion (~7% 1-heptene conversion based on the C_{11} yield), the ratio of 1-hexene to C_{11} olefins produced was 3.43/1, demonstrating that ethylene incorporation is approximately 70 times faster than α-olefin incorporation, similar to the case for the previously reported (PNP)Cr system.[26]

Scheme 2

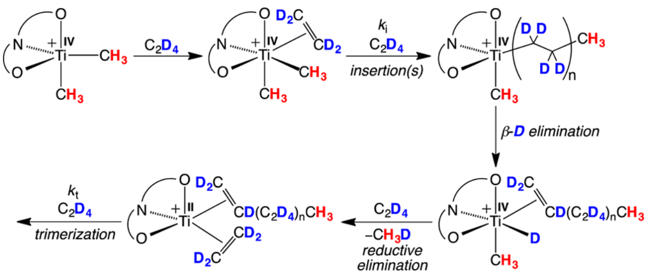


The successful generation of a catalyst by stoichiometric activation facilitates experiments aimed at insight into the mechanism(s) of ethylene trimerization. Monitoring the progress of the reaction by ^{1}H NMR spectroscopy demonstrates that, after addition of ethylene to [(FI)TiMe$_2$][MeB(C_6F_5)$_3$] in C_6D_6/*o*-$C_6H_4F_2$ at room temperature, 1-hexene formation begins rapidly (<15 min); however, at this time the signals corresponding to the precatalyst [(FI)TiMe$_2$][MeB(C_6F_5)$_3$] have only decreased in intensity by ~25% in comparison with the spectrum acquired prior to ethylene addition.[27] Over a period of several hours, the signals of [(FI)TiMe$_2$][MeB(C_6F_5)$_3$] decrease slowly as ethylene is consumed and 1-hexene/C_{10} olefins are produced, and catalytic activity ceases shortly after [(FI)TiMe$_2$][MeB(C_6F_5)$_3$] is no longer observable by ^{1}H NMR spectroscopy.[20] These observations indicate that the overall rate of trimerization is significantly faster than the rate of initiation and that the rate of catalyst decomposition is comparable to that for initiation.

Room-temperature EPR spectroscopy shows the formation of a Ti^{III} species (g = 1.958) in the reaction of B(C_6F_5)$_3$ with (FI)TiMe$_3$;[28] the yield is ~20% (quantified by double integration relative to Cp$_2$VCl$_2$ as an external standard), which is consistent with the 80% NMR yield of [(FI)TiMe$_2$][MeB(C_6F_5)$_3$] (see above). Upon addition of ethylene, the EPR signal increases during trimerization catalysis, reaching a maximum intensity around 5 times the initial value after 2 h (by which time ~80% of 1-hexene production has occurred) and remaining there for several hours after catalysis has stopped. These observations strongly suggest that the Ti^{III} species is a decomposition product, not an active trimerization catalyst or precatalyst.

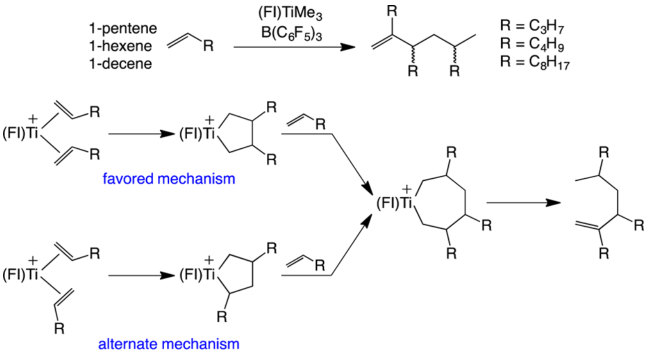
Treatment of [(FI)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] with a 1/1 C$_2$H$_4$/C$_2$D$_4$ mixture at 25 °C produces only four isotopologues of 1-hexene, namely C$_6$H$_{12}$, C$_6$H$_8$D$_4$, C$_6$H$_4$D$_8$, and C$_6$D$_{12}$, which rules out a Cossee type mechanism due to the absence of scrambling and is in accord with the metallacycle mechanism.[29−31] Such a mechanism implicates a reduced species, presumably Ti^{II}; in order to investigate its formation, [(FI)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] was treated with C$_2$D$_4$ at 25 °C. The immediate formation of CH$_3$D was observed by ^{1}H NMR spectroscopy, along with catalytic production of 1-hexene-d_{12}, implying that initiation proceeds via a sequence of initial ethylene (C$_2$D$_4$) insertion(s) into Ti−CH$_3$, followed by β-D elimination and reductive elimination of CH$_3$D, which gives the aforementioned Ti^{II} species (Scheme 3). We have not yet been able to observe any corresponding α-olefin (e.g., CH$_3$CD═CD$_2$); most likely it is incorporated in the first trimerization cycle, which can give several different C$_7$ olefins. Furthermore, if the rates of ethylene insertion and β-H elimination are similar, olefins higher than propylene would be involved in the first trimerization cycle, making it difficult to experimentally observe these products. These results, along with the slow rate of initiation (see above), suggest that the slow step in this system is the initial insertion of ethylene into a Ti−Me bond of the cationic titanium dimethyl complex. Previous DFT calculations for a related system ([(Ph(CMe$_2$)Cp)TiMe$_2$]$^+$)[19] predict an initiation pathway that involves methane elimination, in accord with our experimental observations.[32]

Scheme 3



[(FI)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] is also a precatalyst for the selective trimerization of LAOs, affording trimers in greater than 95% selectivity at 25 °C, with TONs of ca. 350 for 1-pentene and 1-hexene and ca. 100 for 1-decene (Scheme 4). Even more remarkably, among the trimers produced, ca. 85% are one regioisomer, strongly suggesting a single site active catalytic species.[20] The major olefin product is proposed to form by a tail-to-tail coupling, followed by 1,2-insertion and selective β-H elimination (favored mechanism, Scheme 4). However, it is possible that a head-to-tail coupling occurs first, followed by selective 1,2-insertion into the more substituted segment of the metallacycle and selective β-H elimination (alternate mechanism, Scheme 4). Although we cannot distinguish between these two pathways at this point, we favor the former in light of the propensity for metallacyclopentanes to form tail-to-tail dimers,[33] while the alternate pathway requires a 1,2-addition of the third olefin into the more sterically encumbered side of the metallacycle.

Scheme 4



In conclusion, [(FI)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] is a precatalyst for selective olefin trimerization. This stoichiometrically activated catalyst system facilitates mechanistic studies, which demonstrate that catalyst activation occurs via ethylene insertion(s), followed by β-H elimination and reductive elimination of methane, to form the active Ti^{II} catalyst. Most importantly, [(FI)TiMe$_2$][MeB(C$_6$F$_5$)$_3$] can oligomerize LAOs to trimers with extremely high selectivity, giving 85% of a single regioisomer, offering the potential for upgrading inexpensive and readily available feedstocks to value-added products, such as diesel/jet fuel and lubricants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving experimental details, characterization data, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare the following competing financial interest(s): A provisional patent application partially based on this work has been filed.

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