Chapter 4

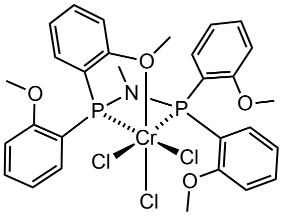
Improved Synthesis of Fujita’s Ti Phenoxy–Imine Catalyst and Initial Studies of 1-Hexene Trimerization

Chapter 4

Introduction

α-Olefins are important building blocks for many valuable products including detergents, polymers, and lubricants.[1] Currently, the primary industrial route to even carbon number α-olefins is oligomerization of ethylene, which generates a statistical mixture (Schulz–Flory distribution) of olefins. For many applications, however, a pure olefin feedstock is required, such as in copolymerizations of 1-hexene and ethylene to generate linear low density polyethylene (LLDPE);[2] thus, costly fractional distillation is often necessary to separate olefin products generated through nonselective oligomerization.[3]

Selective trimerization of ethylene and other olefins by homogeneous catalysts may offer a more cost effective route to obtain some linear α-olefins. Indeed, interest in this field has grown and selective olefin oligomerization systems are now known for chromium, titanium, and tantalum, with Cr systems generally being the most active and selective.[4] For example, a PNP/$CrCl_3(THF)_3$ (PNP = *N*,*N*-bis(bis(*o*-methoxyphenyl)phosphino)methylamine) is known that can be activated with 300 equiv of MAO at 20 atm ethylene and 80 °C to produce 90% C_6 with 99.9% 1-hexene with a productivity of 1,033,200 g (g of Cr)$^{-1}$ h^{-1} (Figure 4.1).[5] In fact, a chromium system is currently used by Chevron–Phillllips for the commercial production of 1-hexene.[6]

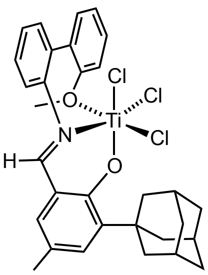


90% C_6 (99.9% 1-hexene)
1.8% C_8
8.5% C_{10}
1033200 g (g Cr)$^{-1}$ h^{-1}
20 bar, 80 °C, 1 h

Figure 4.1 PNP/$CrCl_3(THF)_3$ system for selective ethylene trimerization. See ref. 5.

Our group is interested in upgrading simple feedstocks to liquid hydrocarbon fuels through co-oligomerization of heavy and light olefins. An ideal catalytic system for this process would be selective for fuel range hydrocarbons, which for diesel fuel is typically C_8–C_{18}. If a catalyst could trimerize a potentially renewable feedstock such as ethylene and then subsequently incorporate the resulting α-olefin product effectively into new catalytic cycles, then a selective route to hydrocarbons larger than C_6 or C_8 could be obtained using a simple feedstock as a starting material.

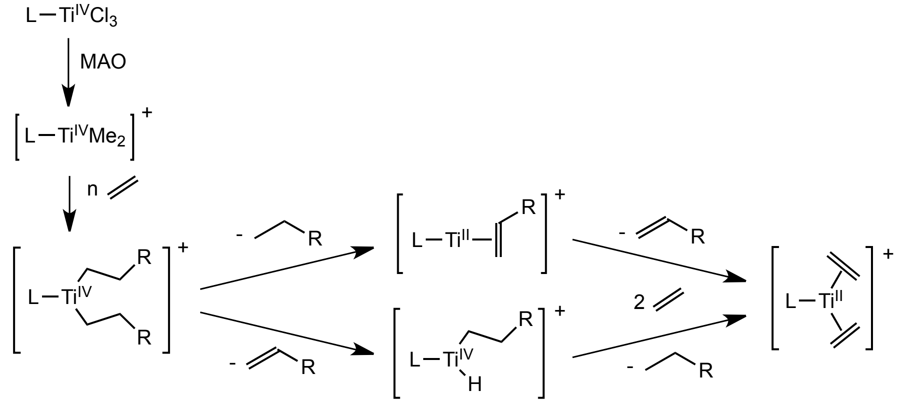
Recently, Fujita and co-workers reported a Ti complex supported by a phenoxy–imine (FI) ligand with a pendant donor arm that upon activation with methylaluminoxane (MAO) trimerizes ethylene to 1-hexene with excellent activity and selectivity (Figure 4.2).[7] Fujita proposes selective trimerization involves a metallacycle mechanism with Ti(II) and Ti(IV) species, rather than linear chain growth (Cossee-Arlman mechanism). β-hydride elimination and reductive elimination are proposed to form an intermediate Ti(II) species from a starting Ti(IV) dialkyl species (Scheme 4.1). This proposed Ti(II) intermediate species can then oxidatively couple ethylene to form a Ti(IV) metallacyle, which can insert another ethylene to form a metallacycloheptane. β-hydride elimination and reductive elimination or a concerted 3,7-H transfer from the metallacycloheptane intermediate leads to 1-hexene (Scheme 4.2). Indeed, studies in our laboratory using deuterium labeled ethylene (C_2H_4 and C_2D_4) have confirmed a metallacycle mechanism;[8] only products with even numbers of deuterium were observed to form when a 1:1 mixture of C_2H_4 and C_2D_4 were trimerized (a Cossee-Arlman mechanism is expected to lead to products with odd numbers of deuterium).



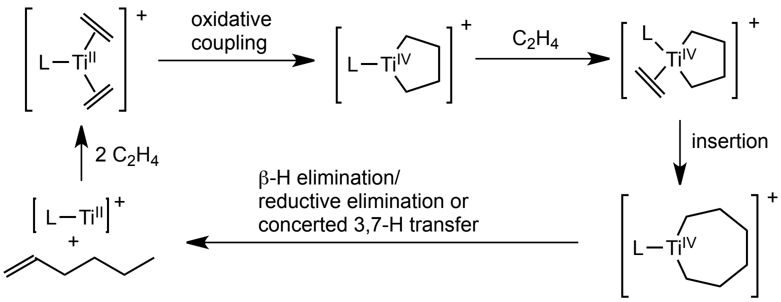
0.5% PE
93.9% C_6
5.6% C_{10}
2720 kg (g Ti)$^{-1}$ h^{-1}
32 bar, 30 °C, 1 h

0.4% PE
92.3% C_6
7.3% C_{10}
7140 kg (g Ti)$^{-1}$ h^{-1}
50 bar, 30 °C, 1 h

Figure 4.2 Trimerization of ethylene with a (FI)Ti complex at different ethylene pressures. See ref. 7.



Scheme 4.1 Proposed mechanism for formation of Ti(II) from starting Ti(IV) complex upon activation with MAO. (Adapted from ref. 7).



Scheme 4.2 Proposed mechanism for selective trimerization of ethylene to 1-hexene by (FI)Ti complexes. (Adapted from ref. 7).

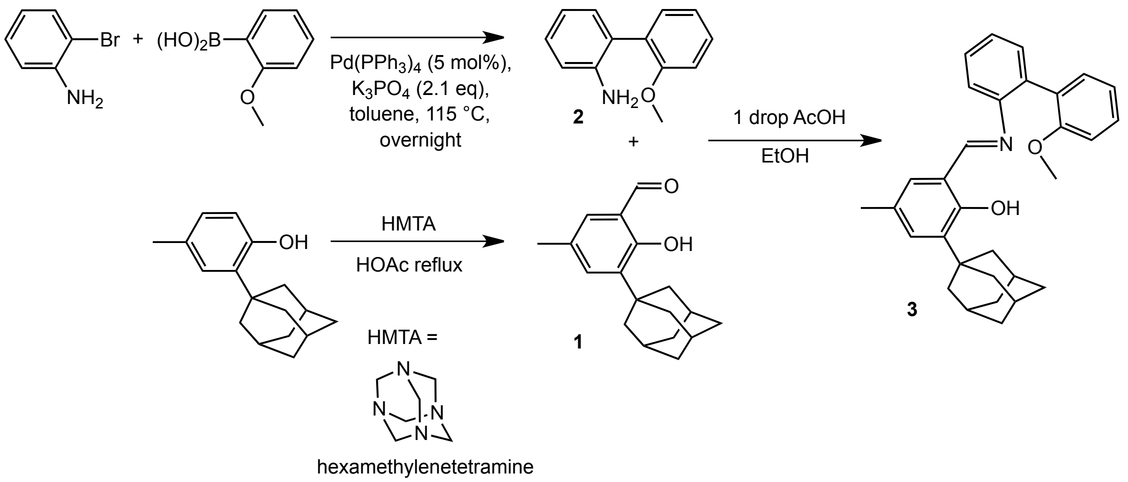
Interestingly, Fujita reports the formation of C_{10} products during the trimerization of ethylene with (FI)Ti complexes. These products result from incorporation of newly formed 1-hexene into the ethylene trimerization catalytic cycle. Furthermore, Fujita has identified primarily one major C_{10} product: 2-butyl-hex-1-ene, with only minor branched decene products, which may suggest that 1-hexene is incorporated selectively. Based on these results, we were interested in investigating (FI)Ti complexes as potential candidates for trimerization of higher α-olefins for selective formation of fuel range liquid hydrocarbons.

Results and Discussion

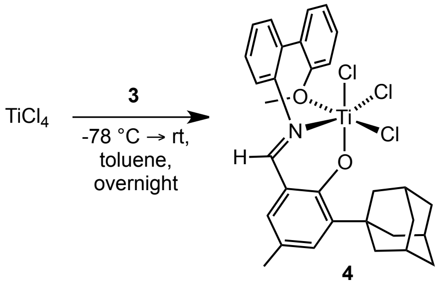
Improved Synthesis of Fujita Catalyst

The synthesis for phenoxy–imine ligand reported by Fujita et al., seemed unnecessarily cumbersome, so we first sought to design a more straightforward syntheis that would also be easier to scale up. Formylation of 2-adamantyl-*p*-cresol[9] was achieved via a Duff reaction with hexamethylenetetramine (HMTA) in refluxing acetic acid to yield 3-admantyl-2-hydroxy-5-methylbenzaldehyde **1**

(Scheme 4.3).[10] For comparison, Fujita employed a magnesium-mediated ortho-formylation reaction, which requires more steps and is less amenable to large-scale reactions.[7,11] The aniline 2-(2'-methoxyphenyl)aniline **2** was synthesized by a Suzuki coupling reaction between commercially available 2-bromoaniline and 2-methoxyphenylboronic acid. In our hands, the Suzuki coupling reaction conditions reported by Fujita and co-workers did not lead to any C–C bond coupling;[7] for our conditions, see the Experimental Section. Finally, a condensation reaction between **1** and **2** led to the desired phenoxy–imine ligand **3** (Scheme 4.3). Metalation of **3** with $TiCl_4$ in toluene yielded the Ti phenoxy–imine complex (**3**)$TiCl_3$ **4** (Scheme 4.4). Notably, we did not observe precipitation of **4** from the reaction mixture as described by Fujita et al.,[7] but were able to obtain complex **4** by removal of solvent in vacuo and washing the solid with diethyl ether.



Scheme 4.3 Improved synthesis of phenoxy–imine ligand **3**.



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Scheme 4.4 Synthesis of (FI)Ti complex **4**.

Trimerization of 1-Hexene in Different Solvents and Neat

We were interested in testing the ability of **4** to trimerize linear α-olefins higher than ethylene. We have previously observed significant solvent effects on trimerization activity for a Cr trimerization precatalyst [$CrCl_3$(PNP)].[12] Thus, we were interested in investigating the potential of **4** to trimerize 1-hexene in different solvents. For our initial investigations, we tested activation of **4** with 1000 equivalents of MMAO in cyclohexane – the solvent used for ethylene trimerization studies by Fujita – and chlorobenzene. Unfortunately, at somewhat dilute concentrations of 1-hexene (~0.2 M) in either cyclohexane or chlorobenzene, we observed disappointing productivities for 1-hexene oligomerization: 2.7 g of C_{12} + C_{18} (g of Ti)$^{-1}$ h^{-1} and 17.1 g of C_{12} + C_{18} (g of Ti)$^{-1}$ h^{-1}, respectively. By comparison, the reported productivity of **4** for ethylene trimerization under only 7.9 atm of ethylene is 155 kg of 1-hexene (g of Ti)$^{-1}$ h^{-1} (productivity is dependent on ethylene pressure). Since we still observed some conversion of 1-hexene to C_{12} and C_{18} products, we decided to test trimerization of neat 1-hexene; activation of **4** with 1000 equiv of MMAO led to oligomerization of 1-hexene with a productivity of 730 g of C_{12} + C_{18} (g of Ti)$^{-1}$ h^{-1}. Analysis of the oligomerization products by GC suggests that at least five different C_{18} products formed and indicates that more C_{18} products formed than C_{12} products: 0.29 g and 0.01 g, respectively (Figure 4.3). Notably, eight different C_{18} products are possible, which may indicate that the formation of some products are unfavorable or the products may not be sufficiently separated by GC (see Scheme 4.5 for all possible C_{18} products).

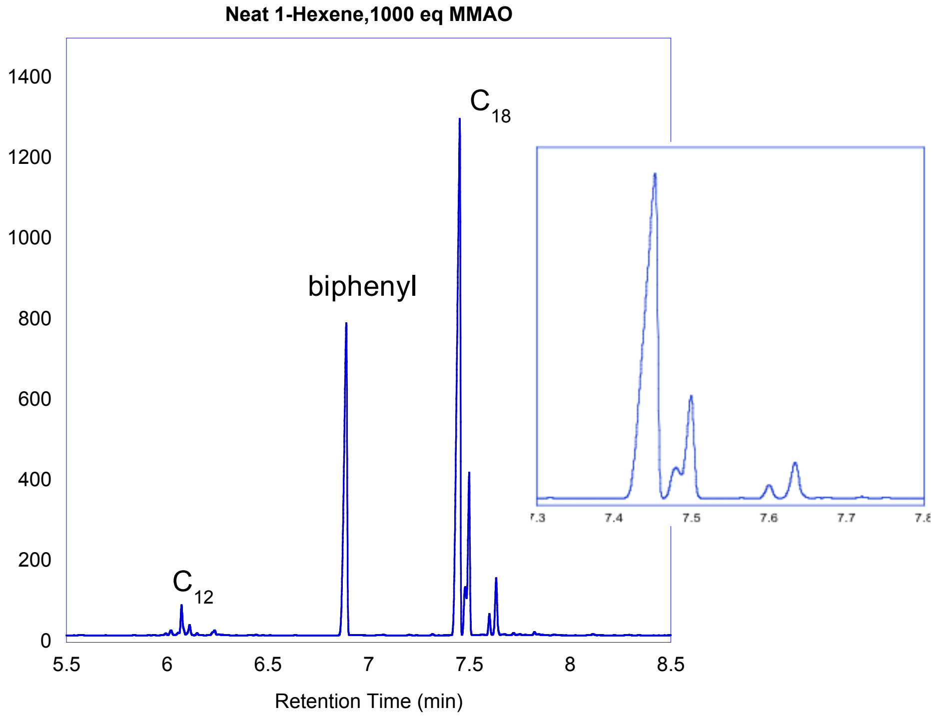
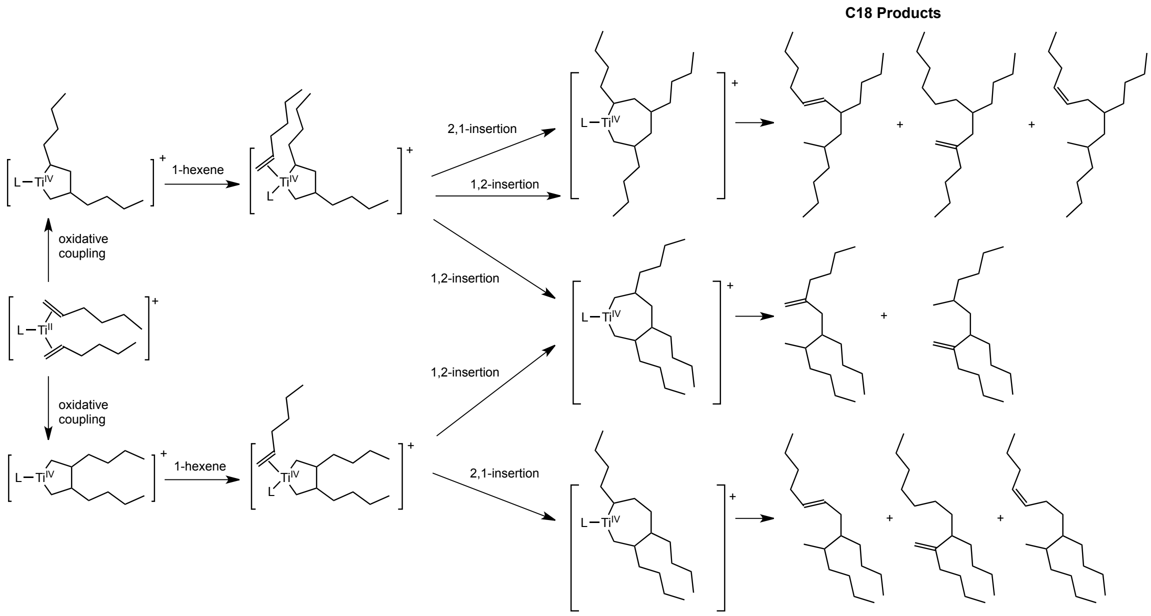


Figure 4.3 GC trace of 1-hexene oligomerization products from **4**/MMAO with close-up of C_{18} product peaks (biphenyl is an internal standard).



Scheme 4.5 Possible C_{18} products from trimerization of 1-hexene.

Investigation of MAO Equivalents

In the initial ethylene trimerization report, Fujita employs a rather high Al/**4** ratio of 10,000:1. We were interested in investigating the effect of different ratios of Al (MMAO)/**4** on oligomerization activity and to determine if less MAO could be used in the reaction. Accordingly, oligomerization of neat 1-hexene was tested with Al/**4** ratios of 250:1 and 5000:1. These data along with the data for 1000:1 are shown in Table 4.1. The productivity of the reaction was significantly lower when only 250 equiv of MMAO were employed: 4.5 g of C_{12} + C_{18} (g of Ti)$^{-1}$ h^{-1}; however, the productivity did not significantly increase upon increasing the MMAO equivalents from 1000 to 5000. These results suggest that 1000 equiv of MMAO may be sufficient for activation of **4** for oligomerization.

Table 4.1 Data for trimerization of 1-hexene with different equivalents of MMAO.

1-Hexene Concentration[a]	MMAO (equiv)	Selectivity (g product)		C_{12} and C_{18} productivity ((g of C_{12} + g of C_{18})/(g of Ti)·h)
		C_{12}	C_{18}	
neat	250	4.9×10^{-4}	1.4×10^{-3}	4.5
neat	1000	1.0×10^{-2}	2.9×10^{-1}	750
neat	5000	5.0×10^{-2}	3.6×10^{-1}	962

[a]Oligomerization were carried out with1 mL of PhCl at 22 °C for 1 h.

Conclusions and Future Work

An improved synthesis of the phenoxy–imine ligand reported by Fujita has been described and oligomerization of 1-hexene by a (FI)Ti complex is reported. Oligomerization of 1-hexene was found to be inefficient at dilute concentrations of 1-hexene, but C_{12} and C_{18} products were observed to form with good productivities when 1-hexene was used as the solvent. The influence of Al equivalents on oligomerization productivity was also investigated. Although these results represent only preliminary data, they importantly indicate that the (FI)Ti complex **4** can trimerize higher α-olefins, which is promising for the development of a catalytic system to upgrade light olefins into liquid fuel range hydrocarbons. Future experiments will investigate the catalyst lifetime, as well the rate of incorporation of linear α-olefins (e.g. 1-heptene) vs. ethylene.

Experimental Section

General Considerations

All air- and moisture-sensitive compounds were manipulated using standard high-vacuum and Schlenk techniques or manipulated in a glovebox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl and stored over titanocene where compatible, or dried by the method of Grubbs.[13] 3-admantyl-2-hydroxy-5-methylbenzaldehyde (**1**) and **3** were prepared following literature procedures.[10] 2-adamantyl-*p*-cresol, hexamethylenetetramine (HMTA), 2-bromoaniline, 2-methoxyphenylboronic acid and $TiCl_4$ as a 1.0 M solution in toluene were purchased from Sigma Aldrich and used as received. Modified methylaluminoxane (MMAO) was purchased from Albemarle as a 7 wt% Al solution in isohexanes (MMAO-C4). 1-Hexene was distilled from CaH_2. C_6D_5Cl and $CDCl_3$ were purchased from Cambridge Isotopes. C_6D_5Cl was distilled from CaH_2 and passed through a plug of activated alumina prior to use. NMR spectra were recorded on Varian Mercury 300, Varian INOVA 500 or Varian INOVA 600 spectrometers and referenced to the solvent residual peak. Gas chromatography–mass spectrometry (GC-MS) analyses were performed on an Agilent 6890N system with an HP-5MS capillary column (30 m length, 0.25 mm diameter, and 0.5 μm film) that was equipped with an Agilent 5973N mass selective detector. Gas chromatography (GC) analyses were performed on an Agilent 6890N instrument with a flame ionization detector (FID). Routine runs were performed using a DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm film) with the following heating program: hold at 40 °C for 3 min, ramp temperature at 50 °C/min to 290 °C and then hold for 3 min (total run time 13 min). The amount of products in each oligomerization experiment was determined by comparison of the integrated areas of the peaks to the integrated area of a biphenyl internal standard as a reference.

2-(2’-methoxyphenyl)aniline 2. An oven-dried 350 mL Schlenk bomb was charged with a stirbar, evacuated and refilled with Ar. Under positive Ar pressure, 2.955 g (0.0171 mol) of 2-bromoaniline, 2.871 g (0.189 mol) 2-methoxyphenylboronic acid, 0.998 g (0.864 mmol) of $Pd(PPh_3)_4$ and 10.933 g (0.515 mol) of K_3PO_4 crushed with a mortar and pestle were added and the vessel was sealed with a septum. The vessel was evacuated and refilled with Ar three times. 70 mL of dry toluene was added via syringe and the vessel was sealed with a Kontes valve. The reaction mixture was stirred at room temperature for 2 min, then the vessel was placed in a 115 °C oil bath overnight. The following day the vessel was cooled to room temperature, and the suspension filtered through celite with the aid of dichloromethane . Solvent was removed in vacuo and the resulting residue was purified by column chromatography on silica gel using 5:1 hexanes/ethyl acetate as the eluent to afford **2** as a white solid. 2.568 g (0.0129 mol) yellow-white powder (75% yield). The identity of the compound was confirmed by comparison with the reported spectroscopic data.

Modified Procedure for Synthesis of (3)TiCl$_3$ 4. A toluene solution of **3** was added via cannula to a solution of $TiCl_4$ in toluene at -78 °C under Ar on the Schlenk line. The reaction mixture was allowed to warm to room temperature and stirred overnight. No solid was observed to precipitate, so the solvent was removed *in vacuo* to reveal a red-brown sludge, and the reaction vessel was taken into a glovebox. The sludge was taken up in diethyl ether and filtered through a glass frit to reveal a red brown powder. The identity of the compound was confirmed by comparison with the reported spectroscopic data.

General Procedure for Oligomerization Reactions in Neat 1-Hexene. To a 20-mL vial in the glovebox was added 4.0 mL (0.032 mol) of 1-hexene and 0.579 g (1000 eq) of MMAO. 5.2 mg (0.0086 mmol) of **4** was dissolved in 1.0 mL of chlorobenzene and taken up into a syringe and then added slowly to the solution of 1-hexene and MMAO while stirring. The vial was capped and stirring was continued at room temperature for 1 h. The reaction was then removed from the glovebox and quenched with a 10% v/v HCl/H_2O solution, then 50.0 mg (0.32 mmol) of biphenyl was added to the reaction mixture as a GC standard. The organic layer was carefully separated and a 2.0 mL aliquot of the organic phase was filtered through a short silica plug and then subjected to analysis by GC.

General Procedure for Oligomerization Reactions with 1-Hexene and a Co-Solvent. The same procedure as above for neat 1-hexene was followed, except 0.210 g of 1-hexene (2.5 mmol) and 10.0 mL of the co-solvent (cyclohexane or chlorobenzene) were added to the MMAO solution.

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