Mechanistic Study of Ester Olefinations Using Dimethyltitanocene

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Olefination of esters using dimethyltitanocene is proposed to proceed via the titanium carbene, $Cp_2Ti{=}CH_2$, on the basis of the following evidence: (1) No H/D exchange or ^{13}C scrambling occurs in the reactions of ethyl acetate or dodecyl acetate using either labeled ester or labeled dimethyltitanocene, (2) kinetics are zero order in ester and first order in Cp_2TiMe_2, (3) the reactions of ethyl acetate and dodecyl acetate with $Cp_2Ti(CD_3)_2$ produce substantial kinetic isotope effects of 9−10, (4) esters of differing electronic and steric environments have similar reactivity, and (5) there is regiochemical preference for the least stable exo-methylene product. These findings are inconsistent with the methyl addition mechanism proposed in the literature.

Introduction

Esters, ketones, amides, and other carbonyl compounds can be methylenated using three different titanium-based reagents: the Tebbe reagent **1** derived from titanocene dichloride and trimethylaluminum,[1] Grubbs' titanacyclobutanes derived from the Tebbe reagent and olefins,[2] and dimethyltitanocene, an old reagent shown recently by Petasis to be effective for olefinations.[3] As indicated by Pine's review on the use of the Tebbe reagent,[4] which includes 201 references, this type of reagent has a wide use in synthetic organic chemistry. Olefinations using dimethyltitanocene are particularly attractive since the reagent is nonpyrophoric and stable to air and water and, therefore, is much easier to prepare and use as compared to the Tebbe and Grubbs reagents. In addition, the Lewis-acidic aluminum of the Tebbe reagent and byproducts of the Tebbe olefination are absent in dimethyltitanocene, which has allowed use of dimethyltitanocene in a wide variety of olefinations involving delicate functionalities, such as silyl esters, anhydrides, carbonates, imides, and acylsilanes.[3b]

Several different mechanisms have been proposed for olefinations with these reagents (Schemes 1 and 2). Grubbs and Pine[5] noted that the reaction of the Tebbe reagent in the absence of base was first order with respect to both the titanium reagent and the ester and had a large negative activation entropy, so they suggested that the ester and Tebbe reagent combined to form a six-membered intermediate (eq 1). In the presence of a base such as pyridine, the reaction was much more rapid and was zero order in ester and first order in titanium reagent,[5] which suggested that the reaction was proceeding through the titanium carbene **2** (eq 2). Reactions involving titanacyclobutanes proceeded with similar kinetics[5] and were also proposed to occur via the carbene (eq 3). On the other hand, Petasis[3a] proposed that the reaction involving dimethyltitanocene proceeded via methyl addition (eq 4, Scheme 2). This proposal[3a] was based primarily on the observation of H/D scrambling in the reaction of protio dodecyl acetate with $Cp_2Ti(CD_3)_2$ and of dodecyl acetate-d_3 with $Cp_2Ti(CH_3)_2$. On the other hand, Petasis has reported no deuterium scrambling in reactions of esters with bis(cyclopropyl)titanocene,[6] and Petasis and Doxsee have provided evidence which suggests that reactions of dimethyltitanocene with alkynes may react via dual pathways depending on reaction conditions, one via the titanium carbene and one via an insertion mechanism.[7,8] Given the very limited and somewhat contradictory results of reactions of the bis(alkyl)titanocenes with esters, the mechanism remains unclear. In order to further probe the mechanism of the reaction, and to determine if the reaction with esters truly follows a mechanism other than the titanium carbene, we have undertaken a detailed kinetic and labeling study. Collectively, our data provide definitive support that the olefination of esters proceeds via the titanium carbene mechanism.

Results and Discussion

Deuterium- and ^{13}C-Labeling Experiments. We initiated our studies using ^{13}C-labeled EtOAc. We chose

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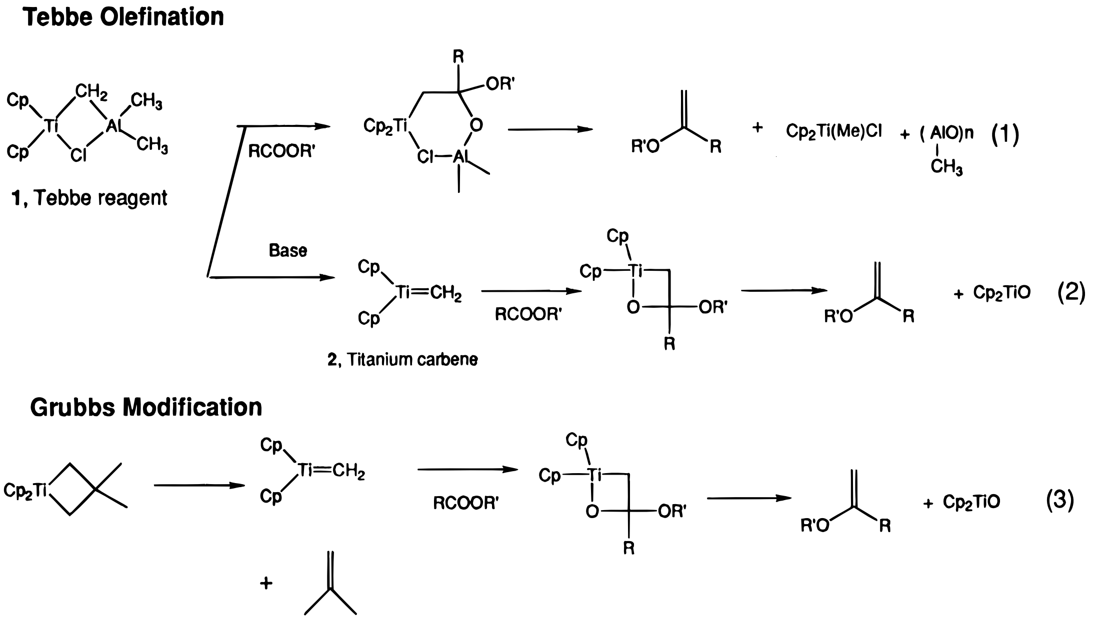
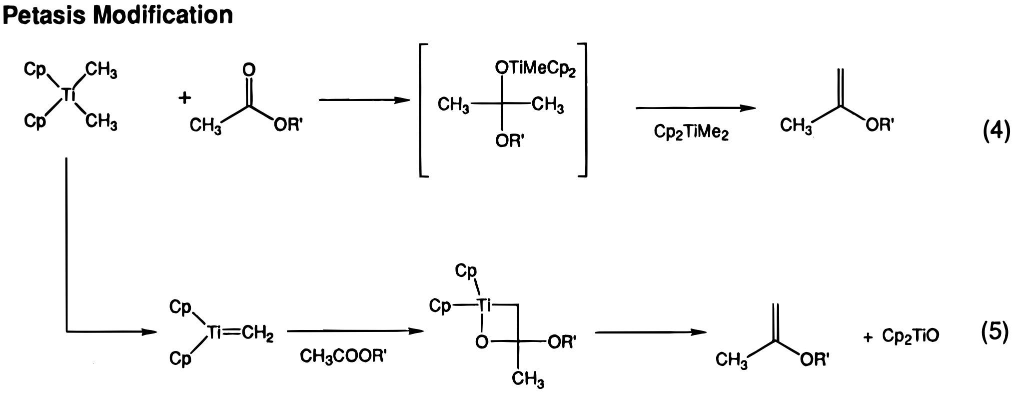
Scheme 1



Scheme 2



the ^{13}C label instead of deuterium initially to avoid the kinetic preference for H vs D in abstractions and the potential problems with D/H exchange with the cyclopentadienyl hydrogens.[9] Reaction of a 0.15 M solution of $^{13}CH_3CO_2Et$ with a 0.45 M solution of $Cp_2Ti(CH_3)_2$ in either toluene or 2:1 toluene:THF at 80 °C gave complete reaction in 4 h. ^{13}C NMR analysis at 1, 2, 4 h time periods showed no detectable ($<1\%$) incorporation of the ^{13}C label into the methylene position (81 ppm) of the vinyl ether product. Since the methyl groups become equivalent in the methyl addition mechanism (eq 4), 50% incorporation of the label would be expected in the methylene position if this mechanism was operating. Six more experiments were run, with three different batches of dimethyltitanocene, with various ranges in concentrations of both dimethyltitanocene and ethyl acetate and with variable reaction times and temperatures. In one case some scrambling of the label was observed. At 50% conversion (1.5 h at 80 °C), 2% scrambling was observed, and 3% scrambling was observed at 90% conversion (3.2 h at 80 °C). Continued heating at 80 °C for 15 h produced 14% ^{13}C scrambling, indicating that the label was being scrambled by a degenerate [1,3]-hydrogen shift. Complete equilibration to 50% scrambled label was achieved after 3 days at 80 °C. This equilibration of the label is most likely occurring by acid catalysis, the source of the acid being residues present on acid-washed glassware. This explanation is supported by the observation that scrambling does not occur to the same extent in all experiments. When the reaction was repeated using 20 mol % pyridine, no exchange was observed even when the reaction was heated for several days at 80 °C. On the other hand, addition of 6 mol % trifluoroacetic acid greatly accelerated the scrambling (13% scrambling in 9 h at 60 °C).

Given these results, we repeated the H/D exchange experiments reported in the literature[3a] using glassware that was not acid-washed. Reacting either EtOAc or dodecyl acetate (0.15 M) with $Cp_2Ti(CD_3)_2$ (0.25−0.45 M) in toluene or 2:1 toluene:THF at 80 °C gave no incorporation of protium in the methylene group of the product. Spiking experiments with reactions using $Cp_2Ti(CH_3)_2$ indicated that incorporation of protium in the methylene position as low as 2% could be readily detected.

These results indicate that the methylenation reaction proceeds without scrambling of the label but that adventitious acid can cause a [1,3]-hydrogen shift that

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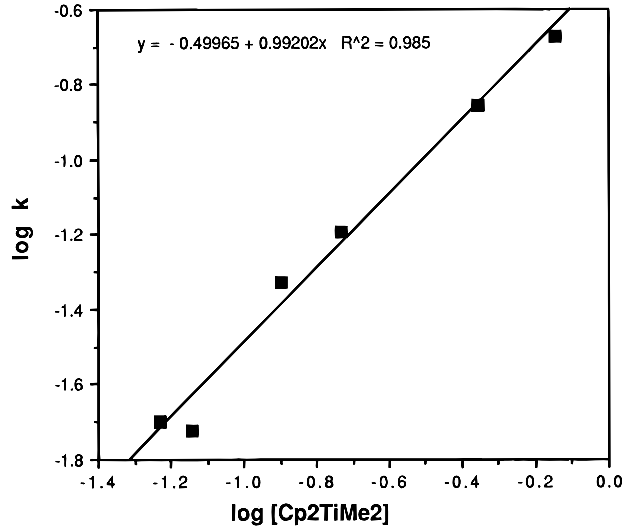


Figure 1. Plot of log k vs log [Cp_2TiMe_2] for the reaction of ethyl acetate with dimethyltitanocene at 60 °C in toluene. The units for the zero-order rate constants are micromoles per minute, while the concentration units are molarity.

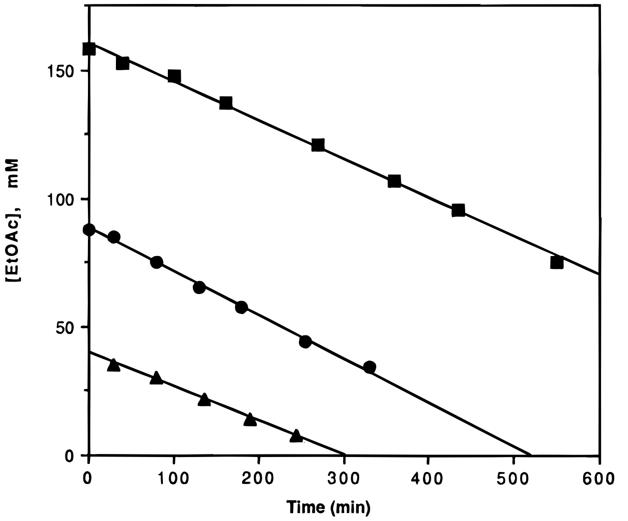


Figure 2. Plot of disappearance of EtOAc (mM) vs time (min) for methylenations using 0.40 M Cp_2TiMe_2 in toluene at 60 °C. Initial concentrations of EtOAc were 158, 88, and 38 mM.

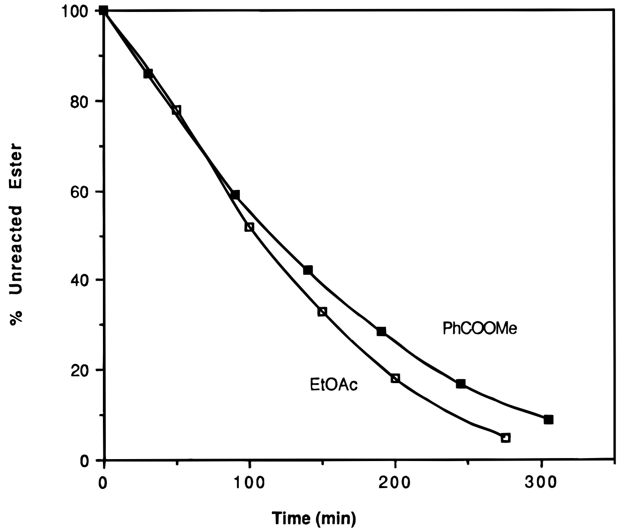


Figure 3. Plot of % unreacted ester vs time for reaction of ethyl acetate and methyl benzoate with dimethyltitanocene at 80 °C in toluene. Initial concentrations were 0.09 M for the esters and 0.25 M for dimethyltitanocene.

scrambles the label as a side reaction. Given these results, which were inconsistent with the methyl addition mechanism, several other mechanistic probes were used to further characterize the reaction.

Kinetics. To determine kinetic orders of the reactants, a series of kinetic experiments was conducted using EtOAc at a concentration of 0.045 M and $Cp_2Ti(CH_3)_2$ concentrations varying from 0.07 to 0.7 M in toluene at 60 °C. The reactions were analyzed by ^1H NMR by integration of the acetyl methyl group of the ester vs the corresponding methyl group of the product. The reactions employing a large excess of the titanium reagent gave a zero-order disappearance of ester. A plot of log k vs log [$Cp_2Ti(CH_3)_2$] (Figure 1) indicated the order in dimethyltitanocene was 1. Another series of reactions was conducted using a constant concentration of dimethyltitanocene (0.40 M) and variable amounts of ethyl acetate (0.038−0.158 M). The zero-order plots for these experiments are shown in Figure 2. Not only does each reaction define a zero-order disappearance of ester but the slopes of each plot are parallel, reinforcing that the reactions are zero order in ethyl acetate.

For the methyl addition mechanism, the reaction would be expected to be first order each in titanium reagent and ester. Instead, the zero-order disappearance in ester indicates the ester is not involved in the rate-determining step, which is consistent with the pathway proceeding through rate-determining formation of the titanium carbene (eq 5).

The rate of reaction of methyl benzoate with dimethyltitanocene to form α-methoxystyrene was also measured. Under conditions that were identical to those used for EtOAc, the rate of reaction was virtually the same (Figure 3). If carbene formation is rate-determining, as suggested by the above kinetics, then all esters would be expected to react at the same rate. On the other hand, EtOAc and $PhCO_2Me$ might be expected to react at different rates, due to electronic and steric differences, if the methyl addition mechanism were operable. The similarity in rates is consistent with the carbene mechanism.

Deuterium Kinetic Isotope Effects. In the reactions using $Cp_2Ti(CD_3)_2$ as discussed above, a large kinetic isotope was noted. Kinetic measurements at 80 °C in toluene revealed a k_H/k_D of 9 (Figure 4) for reactions with dodecyl acetate and 10 for ethyl acetate. These large primary isotope effects are again inconsistent with the methyl addition mechanism, which should exhibit a small secondary effect, and fully consistent with the carbene mechanism with formation of the carbene (loss of methane, CH_4 or CD_4) as the rate-determining step. Since the isotope effects were determined in separate experiments that necessarily used different preparations of dimethyltitanocene (either H_6 or D_6), a control experiment was conducted in which equimolar $Cp_2Ti(CH_3)_2$ and $Cp_2Ti(CD_3)_2$ were used. This experiment revealed an interesting phenomenon in which a statistical distribution of $Cp_2Ti(CH_3)_2$, $Cp_2Ti(CD_3)_2$, and $Cp_2Ti(CD_3)(CH_3)$ was formed, and a subsequent experiment indicated that this exchange also took place with no ester present. On the basis of an NMR analysis with a 20 s delay to ensure accurate quanti-

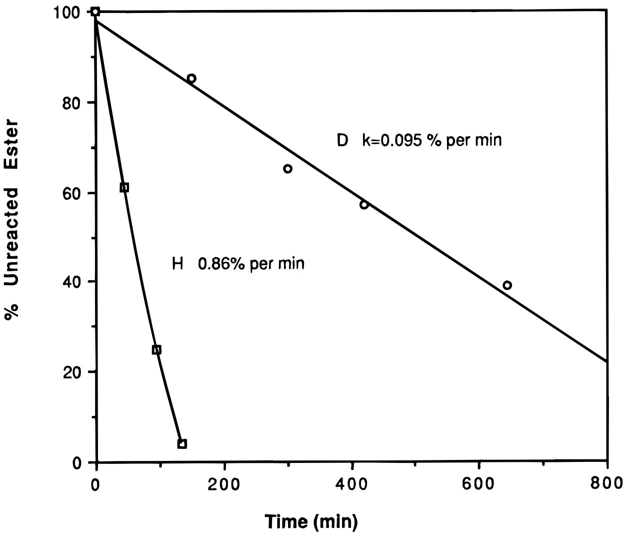
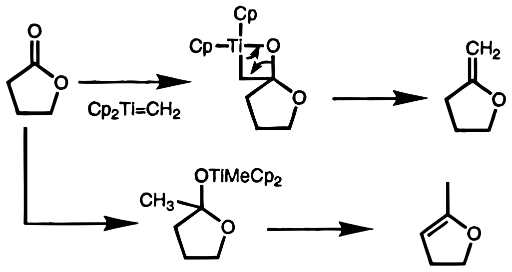


Figure 4. Plot of % unreacted ester vs time for reaction of dodecyl acetate with dimethyltitanocene-h_6 (squares) and dimethyltitanocene-d_6 (circles) in toluene at 80 °C. For both experiments, the initial concentrations were 0.11 M for dodecyl acetate and 0.35 M for dimethyltitanocene.

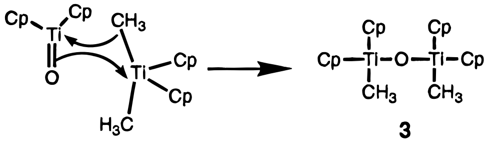
tation, the product of the first experiment indicated that the methylene group contained 16% deuterium, which is consistent with a large isotope effect. No deuterium incorporation occurred in the methyl group, consistent with the lack of scrambling observed before.

Regiochemistry. The regiochemistry observed in appropriate ester substrates can also be indicative of the mechanistic pathway by which the reaction proceeds. For example, in the reaction of γ-butyrolactone with dimethyltitanocene (eq 6),if the methyl addition mechanism was operable, then substantial amounts of the product arising from the most stable endo-double bond would be expected. In contrast, we observed that the exo double bond is formed preferentially by a 99:1 ratio, and the 1% of the endocyclic product is probably formed by isomerization of the exo methylene product since the amount of the endocyclic product continues to grow after the reaction is complete. Petasis has also reported isolating only the exo methylene products in three esters and lactones in which regiochemical choices were available to the reaction[3a] but has observed a small amount of isomerization to the more stable double bond in reactions with bis(cyclopropyl)titanocene.[6] These results are consistent with the carbene mechanism, where the regiochemistry is established by formation of the titanacyclobutane.



(6)

Stoichiometry and Titanium Byproducts. In the reactions of methyl benzoate, ethyl acetate, and dodecyl acetate, the major titanium species observed by NMR and isolated from the reaction mixture after precipitation with hexane was the titanium dimer **3**. At first glance, formation of this species would not appear to support the carbene mechanism, since both methyl groups are ultimately lost in the carbene mechanism with formation of $Cp_2Ti{=}O$ as byproduct, which polymerizes. However, it is known in zirconium chemistry that $Cp_2Zr{=}O$ reacts with Cp_2ZrMe_2 to form the analogous zirconium dimer $Cp_2(Me)ZrOZr(Me)Cp_2$,[10] and the titanocene chemistry would be expected to be the same. A pathway for generation of the titanium dimer is shown in eq 7.



(7)

Since 1 mol of Cp_2TiMe_2 is used to form the titanium dimer byproduct, the stoichiometry of dimethyltitanocene should be 2, which is what is observed experimentally.

Conclusions

The experiments outlined above are consistent with a carbene mechanism for the reaction of dimethyltitanocene with esters, including (1) no H/D exchange or ^{13}C scrambling in the reactions of ethyl acetate or dodecyl acetate with either labeled ester or labeled dimethyltitanocene, (2) kinetics that are zero order in ester and first order in Cp_2TiMe_2, (3) substantial kinetic isotope effects of 9–10 in the reaction of ethyl acetate and dodecyl acetate with $Cp_2Ti(CD_3)_2$, (4) similar reactivity for esters of differing electronic and steric environments, and (5) a bias toward the least stable regiochemical isomer in cases where isomers can be formed.

Experimental Section

General Methods. Toluene-d_8 and tetrahydrofuran-d_8 were obtained in ampules from Aldrich and used without further purification. Toluene, ethyl acetate, and tetrahydrofuran were obtained from EM Science and dried with sieves to a water content of <20 mg/L. Titanocene dichloride and methylmagnesium chloride (3 M in THF) were obtained from Boulder Scientific. Dodecyl acetate, ethyl acetate-2-^{13}C, methyl benzoate, γ-butyrolactone, 4,5-dihydro-2-methylfuran, and methylmagnesium-d_3 chloride (1 M in ether) were obtained from Aldrich and used without further purification. Dimethyltitanocene was prepared from 2.3 equiv of methylmagnesium chloride and titanocene dichloride in toluene/THF as described recently.[11]

Dimethyltitanocene-d_6. Titanocene dichloride (2.49 g, 10.0 mmol) was slurried under nitrogen in toluene (25 mL) and cooled to 4 °C. Methylmagnesium-d_3 chloride (1 M in ether, 30 mL, 30 mmol, 3.0 equiv) was added slowly over 10 min, keeping the temperature below 10 °C. The slurry was stirred for 75 min at 0–5 °C and then quenched over 10 min into 60 mL of ice-cold 6% aqueous NH_4Cl. The layers were separated, and the organic layer was washed with 3 × 60 mL of water and then with 60 mL of brine. The solution was filtered through a pad of magnesium sulfate and then concentrated under vacuum to 25 mL. The solution was flushed with 2 × 70 mL of toluene to remove ether and then concentrated

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to a final weight of 6.83 g. ^{1}H NMR analysis (integration of peaks for toluene methyl group vs Cp groups) indicated a 24.4 wt % solution of dimethyltitanocene-d_6 in toluene (1.67 g, 80% yield), with no residual ether present and no incorporation of protons into the methyl groups.

Kinetic Measurements. All reactions were carried out in 5 mm NMR tubes and followed by ^{1}H NMR spectroscopy at 250 MHz. The NMR tubes were adapted with a Teflon valve to allow introduction of liquids under nitrogen and provide a sealed system once all reactants were added. After the reagents and solvent were weighed into the tube, the solution was degassed by nitrogen sparging for a few minutes. When ethyl acetate was used as a substrate, the degassing was done prior to addition of the ethyl acetate to avoid its evaporation. For rate measurements the NMR tube was immersed in an oil bath controlled at either 61 or 81 °C. Independently, a thermocouple probe immersed in an NMR tube in the oil bath indicated that the internal temperatures were 60 and 80 °C, respectively. The tube was periodically removed from the oil bath for NMR analysis at ambient temperature. For ethyl acetate and dodecyl acetate, the ratios of starting material and product were determined by integration of the acetyl methyl group. A representative kinetic experiment is described below.

Toluene (300 μL), toluene-d_8 (300 μL), and dimethyltitanocene (522 mg of an 18.6 wt % solution in toluene, 0.467 mmol) were charged to a 5 mm NMR tube equipped with a Teflon valve. The solution was sparged with nitrogen for 2 min, during which time 15 mg of toluene was evaporated. Then ethyl acetate (8.9 mg, 0.101 mmol) was added and the tube was immersed in a 61 °C oil bath. NMR spectra were taken at 30, 80, 130, 180, 255, and 330 minutes, and the reaction was monitored by NMR by integrating the acetyl methyl groups of ethyl acetate (1.64 ppm) and ethyl vinyl ether (1.76 ppm). A zero-order rate constant for methylenation of 0.17 mmol/min was calculated, with $R^2 = 0.997$.

^{13}C Scrambling Experiments. Dimethyltitanocene (557 mg of a 15.0 wt % solution in toluene, 0.40 mmol), toluene-d_8 (240 mg), and ethyl acetate-2-^{13}C (11.6 mg, 0.13 mmol) were combined in an NMR tube, and the tube was warmed to 80 °C. The reaction was monitored at 55 min (50% conversion), 105 min (85% conversion), and 140 min (96% conversion) by ^{1}H NMR and ^{13}C NMR. The methylene carbon of the product was a doublet ($J = 7$ Hz) at 81.2 ppm due to coupling with the ^{13}C-labeled methyl group. The combined peak height of the methylene carbon vs that of the ^{13}C-labeled carbon of the methyl group in the product was 1.3%, which is close to that expected (1.1%) for no scrambling, and was also nearly of equal peak height as the two carbons of the ethyl group (60.8 and 15.5 ppm) in which no scrambling was possible. Therefore, it was concluded that the label had scrambled less than 2%. A similar experiment was run with using the same quantities of ethyl acetate and dimethyltitanocene, but toluene-d_8 was replaced with THF-d_8. Monitoring of the reaction over a 4 h time period indicated that the reaction proceeded at a similar rate and provided no evidence for scrambling of the label.

Another experiment was run with added trifluoroacetic acid, which induced scrambling via a [1,3]-hydrogen shift. Dimethyltitanocene (215 mg of an 18.8 wt % solution in toluene, 0.19 mmol), toluene-d_8 (208 mg), toluene (268 mg), and ethyl acetate-2-^{13}C (7.4 mg, 0.083 mmol) were combined in an NMR tube, and the tube was warmed to 60 °C. After 26 h the reaction was 85% complete, and approximately 1% scrambling was evident on the basis of the methylene carbon resonances in the ^{13}C spectrum. While the unscrambled carbon is a doublet ($J = 7$ Hz), the scrambled product with the ^{13}C-labeled methylene is a singlet with a resonance between the doublet of the unscrambled product. Thus, three peaks (centered at 81.16 ppm) of nearly equal size were evident, signifying scrambling on the order of 1% had occurred. After 50 h at 60 °C, scrambling was approximately 2%. Then, 30 μL of a 2% solution of trifluoroacetic acid in toluene (0.6 mg TFA, 0.005 mmol, 6 mol % vs ethyl acetate) was added and the mixture warmed to 60 °C. After 9 h, ^{13}C NMR analysis indicated 13% exchange had occurred, on the basis of the peak heights of the methylene carbon vs the labeled methyl group.

Deuterium Kinetic Isotope Experiments. Two side by side experiments were done, one with protio dimethyltitanocene and with deuterio. Dodecyl acetate (26.4 mg, 0.115 mmol), protio dimethyltitanocene (492 mg of a 15.0 wt % solution in toluene, 0.354 mmol), and toluene-d_8 (284 mg) were combined in an NMR tube and warmed to 80 °C. ^{1}H NMR analysis at 45, 95, and 135 min indicated 39%, 75%, and 96% conversion, respectively. Dodecyl acetate (26.3 mg, 0.115 mmol), deuterio dimethyltitanocene (363 mg of 19.8 wt % solution in toluene, 0.336 mmol), and toluene-d_8 (417 mg) were combined in an NMR tube and warmed to 80 °C. ^{1}H NMR analysis at 150, 300, 420, 645, and 935 min indicated 15%, 35%, 43%, 61%, and 76% conversion.

Product Determination. The products of the four esters (ethyl acetate; dodecyl acetate, γ-butyrolactone, and methyl benzoate) used in these experiments are known and were verified by comparison of proton and carbon NMR spectra. The preparation and isolation of ethyl isopropenyl ether from the reaction of ethyl acetate and dimethyl titanocene is outlined below.

Ethyl acetate (1.33 g, 15 mmol) and dimethyltitanocene (28.9 g of a 21.5 wt % solution in toluene, 30 mmol) were combined and heated at 80 °C for 3 h. NMR analysis at this point indicated 90% conversion. The batch was heated to a boil at 120 °C and distilled through a 10 cm Vigreaux column. The distillate (1.95 g) was collected over a temperature range 60−100 °C and had a composition of 38% ethyl isopropenyl ether (57% yield) and 62% toluene. The sample was redistilled, with 0.30 g of pure ethyl isopropenyl ether collected over a temperature range 59−62 °C (lit.[12] bp 61.9 °C): ^{1}H NMR (CDCl$_3$) δ 1.33 (t, $J = 7$ Hz, 3H, CH_3CH$_2$O), 1.85 (d, $J = 0.6$ Hz, 3H, CH_3C=), 3.74 (q, $J = 7$ Hz, 2H, CH$_3$$CH_2$O), 3.85 (m, 2H, CH$_2$=); ^{13}C NMR (CDCl$_3$) δ 159.8, 81.1, 62.7, 21.5, 14.5.

Isolation and Characterization of the Titanium Dimer 3. The pot residue from the first distillation from the above experiment was treated with 75 mL of hexanes, resulting in precipitation of the titanium dimer, which was filtered out and dried: ^{1}H NMR (CDCl$_3$) δ 5.83 (s, 10H), 0.53 (s, 3H) (lit.[13] ^{1}H NMR (CDCl$_3$) 5.78 and 0.48 ppm); ^{13}C NMR (CDCl$_3$) δ 112.0, 33.5; MS *m/e* 387 (35%), 372 (55%), 178 (100%) (lit.[13] MS *m/e* 387 (50%), 372 (83%), 178 (100%)).

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