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# Selective Catalytic Dimerization of Neohexene by $[Cp^*Ti(NP^tBu_3)Me][B(C_6F_5)_4]$

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The known titanium alkyl cation $[Cp^*Ti(NP^tBu_3)Me][B(C_6F_5)_4]$, supported by a bulky phosphinimide donor, was found to react with 3 equiv of 3,3-dimethyl-1-butene (neohexene) to generate another alkyl cation in which the alkyl group is derived from two dimerized equivalents of the substrate olefin. This species, **1**, was characterized in detail by spectroscopic methods and via X-ray crystallographic determinations of two of its derivatives, the THF adduct (**2**) and the neutral chloride derivative **3** formed upon addition of $Cl^-$ to **1**. Detailed mechanistic experiments suggest **1** is formed via insertion of neohexene into the Ti−Me bond of $[Cp^*Ti(NP^tBu_3)Me][B(C_6F_5)_4]$ to give a detectable intermediate (**4**), which was characterized spectroscopically. Cation **4** reacts in a $\sigma$-bond metathesis reaction with the olefinic C−H bond *trans* to the *tert*-butyl group of another equivalent of neohexene to form an undetected cationic vinyl intermediate, which rapidly inserts a third equivalent of neohexene to generate **1**. Deuterium labeling studies are consistent with this mechanistic picture. Compound **1** is the resting state of a catalytic cycle for dimerization of neohexene; under catalytic conditions (95 °C, [neohexene] = 1.1 M, 1.2−2.1 mol% **1**), clean conversion of neohexene to (*E*)-2,2,5,6,6-pentamethylhept-3-ene was observed, with total turnovers of 44−78.

## Introduction

Titanocenes are a widely explored family of organometallic complexes with applications ranging from those as stoichiometric reagents in organic synthesis[1] to olefin metathesis[2] and coordination polymerization catalyst precursors.[3] In the latter realm, novel catalysts have been developed by replacing one of the Cp donors with isolobal ligands such as amides,[4] alkoxides,[5] ketimides,[6] and phosphinimides.[7] All of these modifications have the effect, to varying degrees, of removing steric bulk from the vicinity of the metal center, while maintaining a threshold of protection necessary for stabilizing active monomeric catalyst species.[8]

In addition to allowing access to very active catalysts, the Cp(L)Ti systems open them to reactivity with a range of sterically more demanding olefinic substrates that are normally unreactive in the bis-Cp manifold. For example, Nomura has explored the ketimide system **I**[9] and the aryloxide catalyst **II**[10] in a wide variety of polymerizations and ethylene copolymerizations with monomers such as styrene, cyclohexene, and other nontraditional polymerization substrates.[11] The greater activity toward substituted olefins is a result of the more open coordination environment about titanium afforded by the removal of steric bulk away from the metal center in ketimide and aryloxide ligands vis-à-vis the Cp ligand.

The Cp and Cp* phosphinimide compounds **III** have been explored extensively by Stephan[7b−d,12] and our group[13] in this light as well. In the course of these studies, we discovered that the Cp* derivative is an effective catalyst for the selective dimerization of neohexene (3,3-dimethylbut-1-ene) to (*E*)-2,2,5,6,6-pentamethylhept-3-ene at moderate temperatures (70−95 °C). While overall turnovers are modest, the reaction is mechanistically intriguing, involving alternating insertion and

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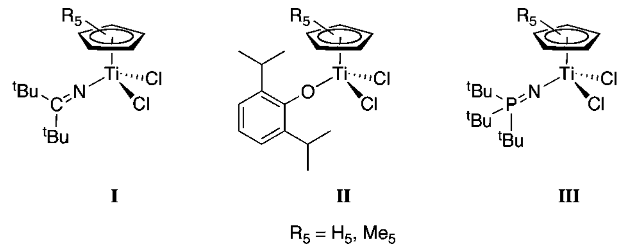
**Chart 1**

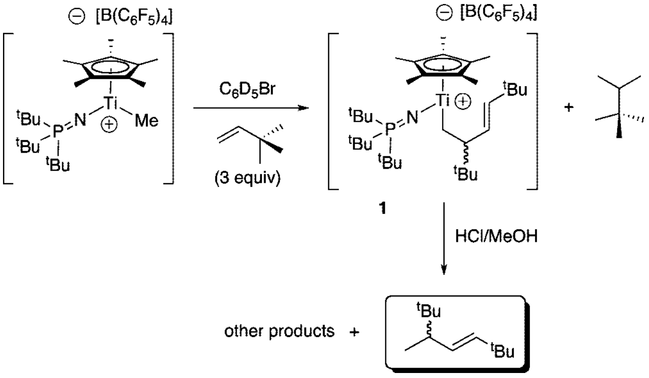


$\sigma$-bond metathesis[14] steps subsequent to initiation using the known alkyl cation $[Cp^{*}Ti(NP^{t}Bu_3)CH_3][B(C_6F_5)_4]$.[7d]

## Results and Discussion

**Synthesis and Characterization of $[Cp^{*}Ti(NP^{t}Bu_3)(C_{12}H_{23})][B(C_6F_5)_4]$ (1).** Reaction of $Cp^{*}Ti(NP^{t}Bu_3)Me_2$ with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in bromo- or chlorobenzene results in rapid methide abstraction to give the previously reported ion pair $[Cp^{*}Ti(NP^{t}Bu_3)Me][B(C_6F_5)_4]$ as an orange-red solution.[7d] Room-temperature addition of an excess (3−4 equiv) of neohexene to the *in situ*-generated ion pair produces an immediate color change from orange to dark red and results in formation of a single titanium-containing product, as determined by $^{31}P\{^{1}H\}$ NMR spectroscopy. Product precipitation with hexanes followed by recrystallization from chlorobenzene/hexanes affords complex **1** as analytically pure red crystals in 85% isolated yield (Scheme 1). Compound **1** was characterized by multinuclear NMR spectroscopy, by elemental analysis, and by the formation of (*E*)-2,2,5,6,6-pentamethylhept-3-ene upon solvolysis with acidic methanol. While 2 equiv of neohexene are incorporated into the alkyl group of cationic **1**, the third was detected as 2,2,3-trimethylbutane by GC/MS and NMR spectroscopy; 1 equiv of this alkane byproduct was generated in the formation of **1**.

**Scheme 1**



$^{1}H$ NMR spectra of **1** in bromobenzene-$d_5$ or dichloromethane-$d_2$ collected at room temperature show significant broadening of the olefin resonances and other signals arising from protons on the alkyl chain, demonstrating that **1** is fluxional in solution. As the temperature of the sample is lowered, the spectra sharpen and $^{1}H$ and $^{13}C$ NMR spectra in dichloromethane-$d_2$ acquired at −75 °C indicate the presence of two diastereomers of **1** in a 19:1 ratio. The spectra provide strong evidence for coordination of the *E* olefinic function to titanium in each of these diastereomers. For example, downfield shifts of the olefin resonances to 134.6/132.1 ppm (major/minor, $C_\gamma$) and 157.1/160.5 ppm ($C_\delta$) relative to those of the free olefin (127.8 and 141.0 ppm for $C_\gamma$ and $C_\delta$ of (*E*)-2,2,5,6,6-pentamethylhept-3-ene, respectively) are observed in the $^{13}C\{^{1}H\}$ NMR spectrum. In the $^{1}H$ NMR spectrum, the alkene proton resonances for $\mathbf{1}_{\mathbf{major}}$ at 6.30 and 6.09 ppm are in the range expected for a metal-bound olefin moiety;[15] the $^{3}J_{HH}$ coupling constant of 16.0 Hz indicates the *E* geometry of this moiety. Diastereomer $\mathbf{1}_{\mathbf{minor}}$ shows a much larger chemical shift difference between olefin resonances (7.57 and 5.33 ppm; $\Delta\delta = 2.24$ ppm, $^{3}J_{HH} = 16.8$ Hz) than $\mathbf{1}_{\mathbf{major}}$, with $H_\delta$ appearing significantly downfield of $H_\gamma$. Similarly large downfield shifts have been observed for the internal vinyl resonances of Zr-tethered alkenes[16a] and have been attributed to the influence of a resonance contributor in which the terminal alkene carbon is bonded directly to the metal, polarizing the alkene and placing a positive charge on the internal olefinic carbon, resulting in the observed downfield shift of the attached proton.[16a,c] This interpretation is supported by structural data showing that, in the absence of $\pi$-back-bonding, tethered olefins typically bind to $d^0$ metals in an asymmetric fashion, resulting in significant polarization of the olefin.[15,17] The disparity in chemical shifts for the alkene protons suggest a similar trend is observed here for $\mathbf{1}_{\mathbf{major/minor}}$. In this system, binding of the olefin to titanium appears to be marginally more symmetric in $\mathbf{1}_{\mathbf{major}}$ than in $\mathbf{1}_{\mathbf{minor}}$ based on the smaller $\Delta\delta$ of alkene resonances observed for $\mathbf{1}_{\mathbf{major}}$ in both $^{1}H$ and $^{13}C$ NMR spectra.

Interconversion of diastereomers $\mathbf{1}_{\mathbf{major/minor}}$ was examined quantitatively by variable-temperature $^{1}H$ NMR spectroscopy.

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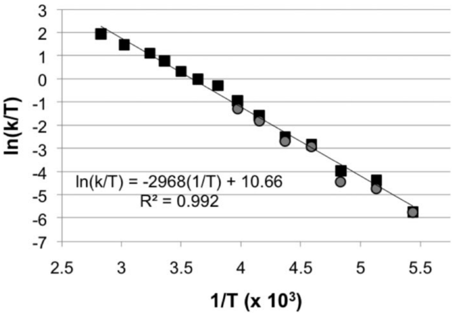


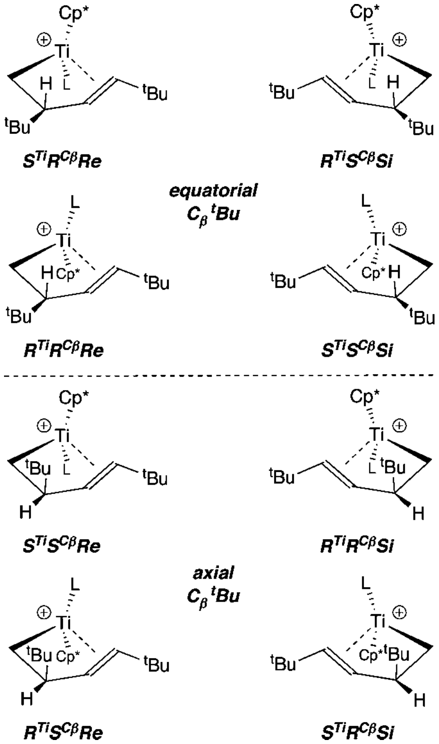
**Figure 1.** Eyring plot for olefin face exchange in ion pair **1** using *k* values obtained from line-shape analysis of VT-NMR spectra. Squares represent data from the $H_\alpha$ and $H_{\alpha'}$ region of spectra; circles were obtained from analysis of the olefin region.

Direct measurement of the barrier to diastereomer interconversion by observation of signal coalescence in the $^1$H NMR spectra was complicated by the large population difference between $\mathbf{1}_{\mathbf{major}}$ and $\mathbf{1}_{\mathbf{minor}}$; the coalescence of the olefinic proton resonances in particular could not be unambiguously identified because of the large chemical shift difference and considerable overlap between coalescing signals. Instead, the rate of interconversion of $\mathbf{1}_{\mathbf{major}}/\mathbf{1}_{\mathbf{minor}}$ was probed by line-shape analysis of the temperature-dependent $^1$H NMR spectra. $^1$H NMR spectra were simulated for unequally populated two-site exchange over the olefin region (−90 to −20 °C) and the $H_\alpha/H_{\alpha'}$ region (−90 to +80 °C), with exchange rates obtained by comparison of calculated and experimental spectra. The results were used to construct the Eyring plot shown in Figure 1. Activation parameters for the exchange process determined from the olefinic region ($\Delta H^\ddagger = 6.1(4)$ kcal/mol, $\Delta S^\ddagger = -26(2)$ cal/mol·K) are in good agreement with values obtained from the α-proton region of the spectrum ($\Delta H^\ddagger = 5.9(2)$ kcal/mol, $\Delta S^\ddagger = -26.0(6)$ cal/mol·K).

Single crystals of **1** were obtained and the solid-state molecular structure of **1** was determined by X-ray diffraction (see Supporting Information). Unfortunately, the precision of this study was limited by severe disorder in the Cp* and tethered alkene ligands even when the data were collected at −150 °C; nevertheless, the structural data collected clearly indicate that the alkyl ligand assumes a conformation about the Cp*(L)Ti girdle that is consistent with coordination of the tethered alkene to the metal.

Given the coordination of this prochiral olefin in the ground-state structure of **1**, and the asymmetry associated with both the Ti and $C_\beta$ centers, there are eight possible stereoisomers of **1**, occurring in four diastereomeric pairs of enantiomers (Scheme 2). As discussed above, we observe only two diastereomers at low temperature; while definitive assignment of the structures of $\mathbf{1}_{\mathbf{major}}$ and $\mathbf{1}_{\mathbf{minor}}$ cannot be made, we presume based on the X-ray results for **1** that the structures that position the $C_\beta$ $^t$Bu group in a pseudoequatorial conformation are favored over those in which it occupies a pseudoaxial position. We tentatively assign $\mathbf{1}_{\mathbf{major}}$ as the $S^{Ti}R^{C\beta}Re/R^{Ti}S^{C\beta}Si$ enantiomeric pair, in which the olefinic $^t$Bu substituent is directed toward the phosphinimide ligand rather than the Cp* donor, whose steric presence is more proximal to the Ti center. The minor diastereomer $\mathbf{1}_{\mathbf{minor}}$ is thus assumed to consist of the $R^{Ti}R^{C\beta}Re/S^{Ti}S^{C\beta}Si$ enantiomers, which differ from $\mathbf{1}_{\mathbf{major}}$ in their configuration at titanium.

**Scheme 2**



Since the configuration of $C_\beta$ is not likely epimerizable under the conditions where the exchange of $\mathbf{1}_{\mathbf{major}}$ and $\mathbf{1}_{\mathbf{minor}}$ is observed, their interconversion likely involves inversion at titanium after dissociation of the coordinated olefin. The average free energy of activation for the exchange process as determined above ($\Delta G^\ddagger(300\ \mathrm{K}) = 13.7(3)$ kcal/mol) is similar to barriers reported for olefin face exchange at several $d^0$ Zr-olefin complexes, which typically fall in the range 10−15 kcal/mol.[16,18] Note that simply dissociating the olefin and invoking face exchange without inversion at Ti also interconverts a pair of diastereomers, but this process leads from an isomer with an equatorial $C_\beta$ $^t$Bu group to one with an axial one. While the rather negative $\Delta S^\ddagger$ value of −26(2) cal/mol·K would seem to argue against a dissociative pathway, the ionic nature of the compound and the polarity of the solvent could be contributing to the entropic barrier to this exchange.

Complex **1** was further characterized by the addition of the donor ligands THF and $Cl^-$, leading to displacement of the alkene group and coordination of the Lewis base to titanium (Scheme 3). In each case, the product consists of a mixture of two diastereomers, as determined by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy. In the case of a neutral donor such as THF, the product is still an ion pair and the 60:40 mixture of diastereomers **2** (220 K) interconvert at room temperature; this therefore is a thermodynamic mixture. For **3**, the ratio of diastereomers is 85:15 and represents a kinetic ratio, since these do not interconvert under any conditions studied. In both products **2** and **3**, the olefin proton resonances for the alkyl ligand move upfield into a chemical shift range consistent with an uncomplexed alkene moiety.

One diastereomer of both complexes were characterized by X-ray crystallography. Isolation of **2** was complicated by its tendency to oil out of solution, but a single crystal of **2** suitable for X-ray crystallographic analysis was eventually grown from $CD_2Cl_2$/hexanes. Recrystallization of **3** from cold hexanes gave crystals suitable for X-ray crystallographic analysis; the molecular structures of **2** and **3** with selected bond distances and angles are shown in Figures 2 and 3, respectively.

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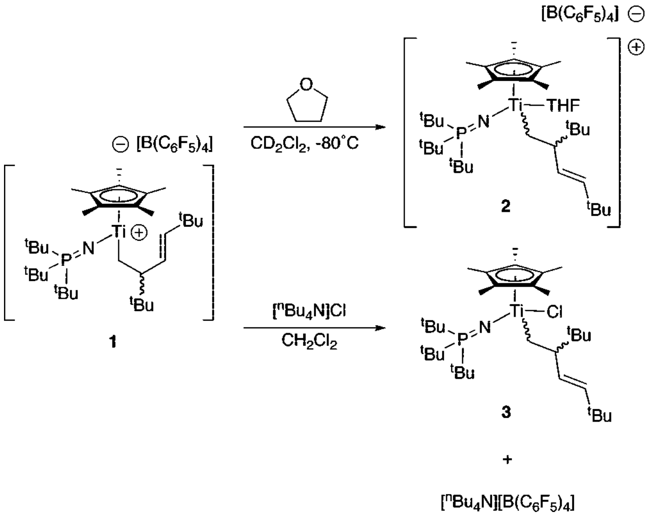
(18) Similar olefin dissociation barriers are observed for cationic titanium complexes with tethered alkenes; see ref 14a.

**Scheme 3**



The coordination sphere around titanium in **2** and **3** is pseudotetrahedral with both complexes displaying similar Ti−N and Ti−C$_\alpha$ bond lengths: 1.805(2) and 2.143(3) Å, and 1.8044(16) and 2.1575(19) Å for **2** and **3**, respectively. The phosphinimide ligand deviates somewhat from the expected linear conformation to give P−N−Ti angles of 169.79(17)° (**2**) and 164.61(10)° (**3**) due to crowding around the titanium center, which compresses the P−N−Ti angle to minimize unfavorable contacts between $^t$Bu$_3$P and the Cp* methyl groups. Widening of C$_\beta$−C$_\alpha$−Ti angles is also observed as a consequence of numerous sterically demanding ligands around the metal center, with a large C$_\beta$−C$_\alpha$−Ti angle of 140.2(2)° observed for complex **2** (129.44(13)° for **3**). By comparison, the related complex CpTi(NP$^t$Bu$_3$)(CH$_2$CH$_2$CH=CH$_2$)Br reported by Stephan et al. has a C$_\beta$−C$_\alpha$−Ti angle of 119.1(5)° and an approximately linear phosphinimide ligand (P−N−Ti = 175.4(3)°).[19]

Both **2** and **3** crystallize as single diastereomers, with both enantiomers present in the unit cell. The quantity of crystals obtained after recrystallization of **3** from hexanes suggested that the solid-state structure obtained corresponded to the major diastereomer observed in solution. This was confirmed by redissolving isolated crystals and recording their $^1$H and $^{31}$P{$^1$H} NMR spectra; resonances that corresponded to the major diastereomer of **3** were observed exclusively. The major diastereomer of **3** depicted in Figure 3 therefore results from replacement of the tethered alkene ligand in the S$^{Ti}$R$^{C\beta}$Re/R$^{Ti}$S$^{C\beta}$Si-configured diastereomer of **1** with chloride. Ion pair **2** also crystallized as the diastereomer derived from direct replacement of the olefin by THF, but our inability to isolate diastereomerically pure **2** in a quantity sufficient for NMR analysis has prevented us from correlating the observed solid-state structure with its corresponding NMR data.

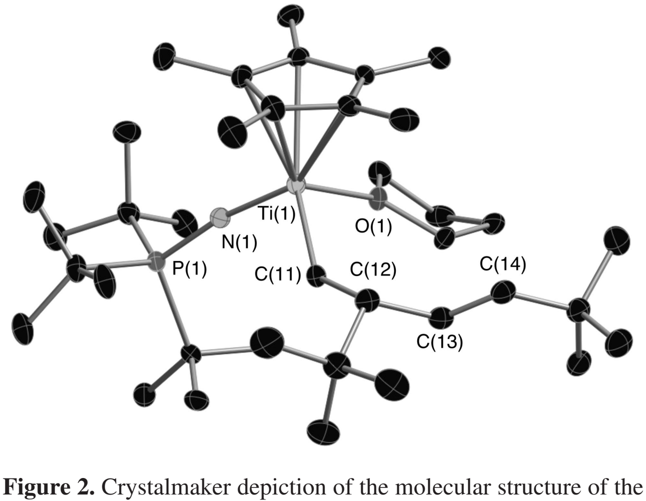


**Figure 2.** Crystalmaker depiction of the molecular structure of the S$^{Ti}$R$^{C\beta}$/R$^{Ti}$S$^{C\beta}$ diastereomer (S$^{Ti}$R$^{C\beta}$ shown) of cation **2** (hydrogens and the anion omitted for clarity). Thermal ellipsoids are drawn at 50%. Selected bond distances (Å): Ti(1)−C(11), 2.143(3); Ti(1)−N(1), 1.805(2); Ti(1)−O(1), 2.081(2); P(1)−N(1), 1.613(2); C(11)−C(12), 1.547(4); C(13)−C(14), 1.328(4). Selected bond angles (deg): N(1)−Ti(1)−O(1), 100.17(10); N(1)−Ti(1)−C(11), 99.57(11); O(1)−Ti(1)−C(11), 99.42(10); P(1)−N(1)−Ti(1), 169.79(17); C(12)−C(11)−Ti(1), 140.2(2).

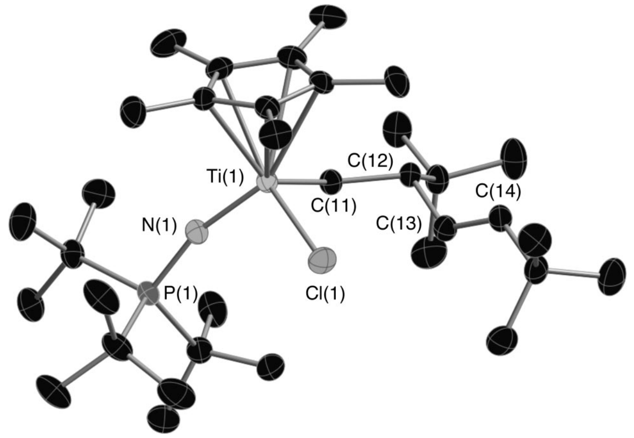


**Figure 3.** Crystalmaker depiction of the molecular structure of the S$^{Ti}$R$^{C\beta}$/R$^{Ti}$S$^{C\beta}$ diastereomer (S$^{Ti}$R$^{C\beta}$ shown) of **3** (hydrogens omitted for clarity). Thermal ellipsoids are drawn at 50%. Selected bond distances (Å): Ti(1)−C(11), 2.1575(19); Ti(1)−N(1), 1.8044(16); Ti(1)−Cl(1), 2.3047(6); P(1)−N(1), 1.5983(16); C(11)−C(12), 1.540(3); C(13)−C(14), 1.322(3). Selected bond angles (deg): N(1)−Ti(1)−Cl(1), 102.38(5); N(1)−Ti(1)−C(11), 96.98(7); C(11)−Ti(1)−Cl(1), 102.58(5); P(1)−N(1)−Ti(1), 164.61(10); C(12)−C(11)−Ti(1), 129.44(13).

**Mechanistic and Deuterium Labeling Studies.** The mechanism by which compound **1** forms was probed via detection of an intermediate and the use of selectively deuterium-labeled substrates. Observation of 1 equiv of 2,2,3-trimethylbutane in the product mixture (Scheme 1) suggested the first step involves 1,2-insertion of neohexene into the Ti−CH$_3$ bond of [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$]. Indeed, monitoring this reaction at −30 °C by low-temperature NMR spectroscopy exposes formation of the ion pair expected from such a step, i.e., [Cp*Ti(NP$^t$Bu$_3$)(CH$_2$CH{Me}$^t$Bu)][B(C$_6$F$_5$)$_4$], **4** (Scheme 4). Loss of the Ti-Me singlet in the proton NMR spectrum of [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$] was accompanied by the appearance of a new doublet resonance at 0.61 ppm, indicating that the methyl group had migrated from titanium to the $\beta$-carbon of an incoming neohexene molecule. Three new multiplets were assigned as H$_\beta$ (2.73 ppm) and the diastereotopic protons attached to C$_\alpha$ (3.79 and 0.07 ppm); coupling patterns (COSY) were consistent with this assignment, although the large disparity in chemical shift for the α-protons is noteworthy and perhaps a result of restricted rotation around the Ti−CH$_2$ bond caused by the steric bulk at titanium.[16a,c] As the temperature of the sample containing **4** and neohexene was raised, resonances in the proton NMR spectrum appeared that were identified with

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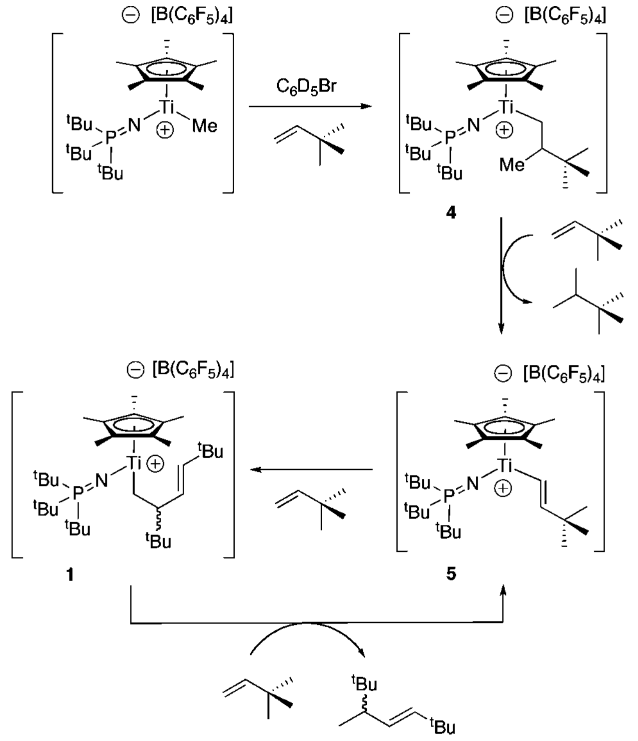
[19] Ti−N and Ti−C$_\alpha$ bond lengths in CpTi(NP$^t$Bu$_3$)(CH$_2$CH$_2$-CH=CH$_2$)Br are similar to those reported here for **2** and **3**: Voth, P.; Fraser, C.; Graham, T.; Zhu, C.; Gauld, J.; Stephan, D. W. *Organometallics* **2006**, *25*, 4779.

**Scheme 4**

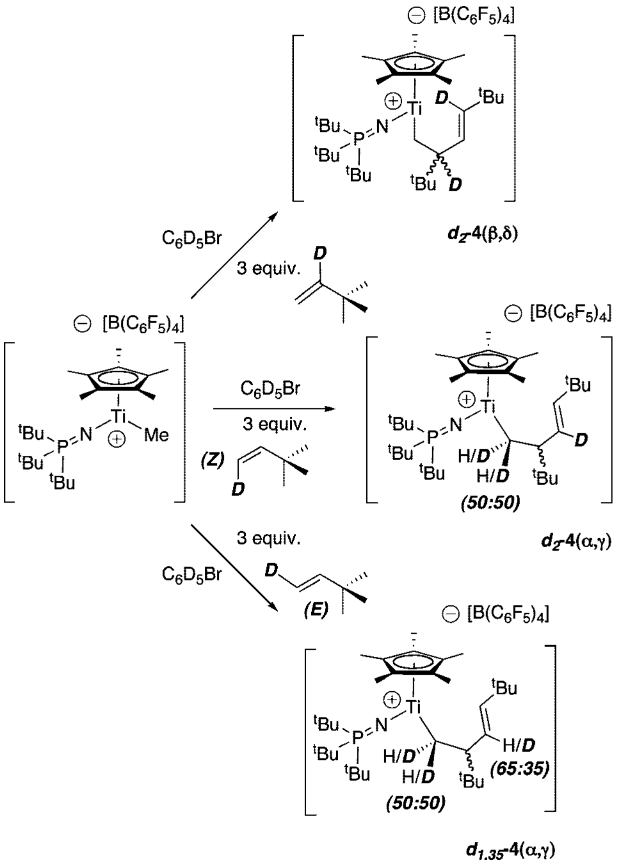


2,2,3-trimethylbutane (1 equiv) and of signals due to product **1**. No other intermediates were observed, which suggests that reaction of **4** with neohexene is the rate-determining step in the formation of **1**. Notably, only the major diastereomer of **1** is observed in the $^1$H NMR spectrum when the reaction is monitored at low temperature, suggesting this is the kinetic as well as the thermodynamic product. Warming the sample to room temperature leads to broadening of the proton resonances caused by alkene dissociation and titanium inversion, which then decoalesce into resonances attributed to the previously discussed diastereomeric complexes $\mathbf{1}_{\mathbf{major}}$ and $\mathbf{1}_{\mathbf{minor}}$ upon recooling in the NMR probe.

These observations are consistent with a mechanism akin to that shown in Scheme 4. Upon warming, alkyl cation **4** reacts with further neohexene in a $\sigma$-bond metathesis reaction to liberate 2,2,3-trimethylbutane and form the vinyl cation **5**. This species is not observed, but we propose it to have the *E* geometry shown since this is the exclusive geometry of the double bond observed in **1**. This cation rapidly inserts another equivalent of neohexene to form **1**.

A similar mechanism has been proposed for the dimerization of ethylene by an electron-poor iridium complex, ($\kappa^2$-*O,O*-acetylacetonate)$_2$Ir(III)(CH=CH$_2$)(Py), which has been shown to proceed through olefin insertion into a metal-vinyl intermediate followed by C−H activation to liberate the dimeric products.[20] The neutral titanium-vinyl complex $Cp_2TiCl(CH{=}CHCH\{R\}C\{CH_3\}_3)$[21] (R = $\{CH_2\}_2Ph$, $CH_2Ph$, $\{CH_2\}_7CH_3$) is also known to be an efficient initiator for polymerization of acetylene to *trans*-polyacetylene even at −40 °C, suggesting that a *cationic* titanium-vinyl complex would be highly reactive toward olefin insertion even at low temperature. Although alkyne addition to the highly substituted titanium-vinyl complex proceeds in a *syn* fashion, rapid isomerization to the more thermodynamically stable *trans* vinyl complex is presumed to occur prior to subsequent acetylene additions. Notably, the addition of substituted alkynes to the neutral titanium-vinyl complex does not result in oligomer formation, but instead results in 2,1-addition of 1 equiv of alkyne to give the (1*Z*,3*E*)-dienyltitanium species $Cp_2TiCl(CR'{=}CHCH{=}CHCH\{R\}C\{CH_3\}_3)$ with high regio- and stereoselectivity; these $\alpha$-substituted complexes are no longer active toward alkyne insertion.

**Scheme 5**



Deuterium labeling studies using selectively labeled neohexenes[22] provide further support for the mechanism shown in Scheme 4, but also reveal some added complexity to the chemistry of these compounds. The results of these experiments are shown in Scheme 5. Most straightforwardly, reaction of $[Cp^*Ti(NP^tBu_3)Me][B(C_6F_5)_4]$ with 2-*D*-3,3-dimethyl-1-butene gives **1** with the deuterium label in the positions expected on the basis of the mechanism in Scheme 4. The (*E*)- and (*Z*)-1-*D*-3,3-dimethyl-1-butene isotopomers, however, deliver labeled **1** in which unexpected scrambling of the label has occurred at $C_\alpha$. For example, reaction with the *Z*-labeled neohexene gives $d_2$-**1** in which the olefinic $C_\gamma$ position is fully labeled, and the diastereotopic $C_\alpha$ positions each are 50% labeled. While the former observation is consistent with selective $\sigma$-bond metathesis involving the C−H bond *trans* to the $^t$Bu group and the Ti−C bond in **4**, the latter is puzzling based on the expectation that concerted olefin insertion into the cationic vinyl intermediate **5** should be stereospecific. Further, in the reaction involving the *E*-labeled neohexene, the $C_\gamma$ position incorporates about 35%

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(20) Olefin isomerization is also observed to give a mixture of 1- and (*E/Z*)-2-butenes: Bhalla, G.; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2005**, *24*, 5499.

(21) Takagi, Y.; Saeki, N.; Tsubouchi, A.; Murakami, H.; Kumagai, Y.; Takeda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2663.

(22) Synthesis of deuterium-labeled neohexene: (a) Igau, A.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2327. Synthesis of $Cp_2ZrHCl$ (Schwartz reagent): (b) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521. (c) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

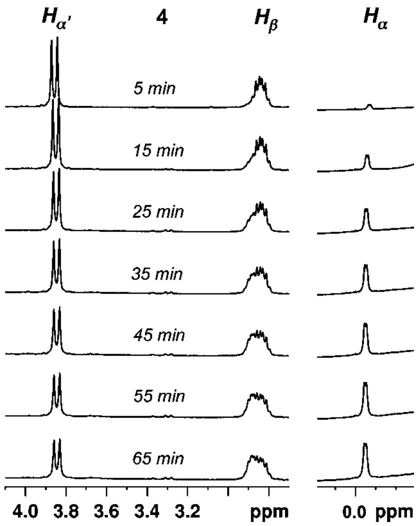

**Figure 4.** Partial $^1$H NMR spectra of the proceeding reaction between [Cp*Ti(NPtBu$_3$)Me][B(C$_6$F$_5$)$_4$] and (*E*)-1-*D*-3,3-dimethyl-1-butene in dichloromethane-$d_2$ at −30 °C. The spectra show the initial appearance of the deuterium label in the $H_{\alpha'}$ position, followed by scrambling of the isotopic label into the $H_\alpha$ position (~50% of isotopic label in each site at 65 min).[23]

deuterium label, while again the $C_\alpha$ positions incorporate ~50% deuterium in each location. When this reaction is carried out at 265 K, the incorporation of D label into $C_\gamma$ falls to about 10%.

We believe we can account for these observations as follows. The scrambling observed at $C_\alpha$ and the unexpected partial incorporation of deuterium label into $C_\gamma$ in the reaction of ion pair [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$] with (*E*)-1-*D*-3,3-dimethyl-1-butene reflect two different processes. The former process appears to involve epimerization at $C_\alpha$; NMR evidence for this was obtained by generating $C_\alpha$-labeled intermediate **4** at low temperature using both (*E*)- and (*Z*)-1-*D*-3,3-dimethyl-1-butene, assuming **4** is a good model complex for **1**.[23] Figure 4 shows a series of partial $^1$H NMR spectra for **4**, depicting the resonances for the two diastereotopic $H_\alpha$ protons and $H_\beta$, taken at 240 K over a period of 1 h during its generation from [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$] and the *E* isotopomer of $d_1$-neohexene;[24] a complementary set of spectra are obtained using the *Z* isotopomer of the olefin. At early reaction times, a spectrum consistent with the stereoselective insertion of the labeled olefin into the Ti−CH$_3$ bond is observed, and the upfield $H_\alpha$ resonance is very low in intensity. Over time, the epimerization occurs, until at 65 min, the two positions are essentially half-occupied with proton, the total integral of the two still equating to that of $H_\beta$. The morphing of the multiplicity in the $H_\beta$ signal reflect this epimerization process.

Three mechanistic possibilities to account for this observation arise. *Effective* epimerization of $C_\alpha$ by epimerization of $C_\beta$ via a $\beta$-hydride elimination/tertiary alkyl mechanism similar to that proposed to account for stereoerrors in polypropylene polymerizations[25] can be ruled out by the lack of any deuterium incorporation into the methyl group of **4**. A second possibility requires isomerization of the (*E*)-$d_1$-neohexene to a mixture of *E*/*Z* isotopomers during formation of **4**. While we do have evidence for such an isomerization process that accounts for the incorporation of deuterium label into the $C_\gamma$ position of **1** noted above (*vide infra*), this process is slow under the conditions that **4** is generated in the current experiment. Furthermore, this is not consistent with the time evolution of the scrambling observed. The last possibility we can envision (and for which we have no strong experimental evidence) involves a reversible deprotonation of $C_\alpha$ by the basic phosphinimide ligand (Scheme 6); the phosphinimine/alkylidene intermediate returns to **4** (or **1**) to produce a 50:50 mixture of isotopomers at $C_\alpha$. Analysis of the spectra indicate that the rate of scrambling from ***S*-$d_1$-4** occurs with a rate of 0.008 ± 0.002 min$^{-1}$, while scrambling from the ***R*-$d_1$-4** is somewhat slower at 0.004 ± 0.003 min$^{-1}$. A difference in rates would be expected given the diastereotopic nature of the $H_\alpha$ and $H_{\alpha'}$, but the precision of these measurements is low enough that they should be interpreted with caution. Nevertheless, the unusual chemical shift dispersion between these two diastereotopic protons in both **4** and **1** may signal latent interaction between a $C_\alpha$ proton and the nitrogen of the phosphinimide. The involvement of α-agostic interactions is not implicated by the spectroscopic data available; the absence of low-frequency C−H stretches in the IR spectrum of **1** and normal $^1J_{CH}$ coupling constants (135−138 Hz) for CH bonds bound to electropositive elements for the α CH groups argue strongly against any ground-state agostic interactions.

The incorporation of deuterium label into $C_\gamma$ in **1** when the methyl cation is treated with an excess of (*E*)-$d_1$-neohexene (Scheme 5) is surprising but reproducible. Closer examination of the spectra obtained in these experiments shows that the excess (*E*)-$d_1$-neohexene partially isomerizes to a mixture that now contains detectable (by $^1$H and $^2$H NMR spectroscopy) amounts of the (*Z*)-$d_1$-neohexene isomer. Whatever the process responsible for isomerization may be, it is slowed considerably at temperatures below 0 °C, where we observe ~10% or less incorporation of D into $C_\gamma$. Since the rate-limiting step in the formation of **1** is the $\sigma$-bond metathesis step converting **4** to **5**, the reaction rate for the *E* isotopomer is likely to be substantially slower than for the *Z* isomer, due to a primary kinetic isotope effect.[26,27] The slower rate for the experiment involving the *E* isomer allows the process that isomerizes the *E* isomer to the *Z* isomer to become competitive, and this *Z* isomer is now also able to engage in $\sigma$-bond metathesis with **4**, producing **5** with a deuterium label in the α-position, which carries through to $C_\gamma$ in the final product **1**.

While the spectroscopic evidence for *E*/*Z* isomerization in the excess labeled olefin is definitive, we do not know what species is responsible for catalyzing the isomerization of pure (*E*)-$d_1$-neohexene to the mixture. Although generation of a Ti-H species would be a viable postulate, given that previous work in our laboratory has demonstrated its accessibility,[12b] we note that it rapidly reacts with bromobenzene via halide abstraction

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(23) Attempts to do similar experiments with low-temperature generation of **1** showed evidence for this epimerization, but the spectra were not as easily interpreted as those for **4**.

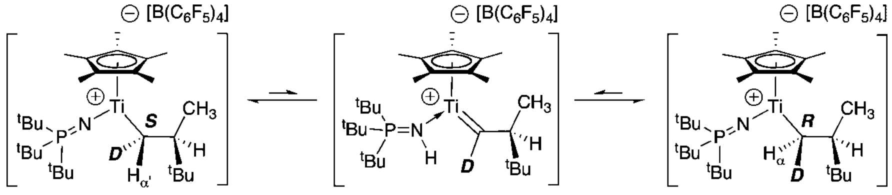
(24) In this experiment, **4** is fully generated after about 40 min; no compound **1** is produced under these conditions, and the only species observed are [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$], the olefin, and **4**. See Supporting Information for a full $^1$H NMR spectrum of $d_1$-**4** from this experiment.

(25) (a) Yoder, J. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 2548. (b) Leclerc, M. K.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **1996**, *118*, 9024. (c) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329. (d) Busico, V.; Cipullo, R. *J. Organomet. Chem.* **1995**, *497*, 113.

(26) An isotope effect of ~2.8 might be expected; see ref 13a.

(27) Measurement of this $k_H/k_D$ proved difficult, but a competition experiment between an equimolar excess of the *E* and *Z* isotopomers of $d_1$-neohexene and [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$], carried out at 0 °C, where the isomerization process mentioned in the main text is minimized, suggests that it is on the order of 3.0(4), on the basis of comparative integrations of the olefinic protons in **1**.

**Scheme 6**



$d_1$-4 $d_1$-4

and *ortho*-metalation pathways under these conditions;[12a] we do not detect any traces of these side products. Furthermore, we do not detect any olefinic byproduct of the $\beta$-H elimination process(es) that would generate such a hydride in any of these experiments. Therefore, we do not favor Ti-H as a likely mediator of this process. However, if formation of **4** is reversible via $\beta$-$CH_3$ elimination,[28] the epimerization process of Scheme 6 may furnish an explanation for this observation.

**Catalysis.** Since **1** is itself a cationic alkyl complex, the possibility that it might turnover via a $\sigma$-bond metathesis step with another equivalent of neohexene was considered. At room temperature, **1** does not undergo reaction with neohexene, but upon warming to 70−95 °C, slow generation of (*E*)-2,2,5,6,6-pentamethylhept-3-ene was observed (Scheme 4). Under catalytic conditions (95 °C, [neohexene] = 1.1 M, 1.2−2.1 mol% **1**), clean conversion of neohexene to (*E*)-2,2,5,6,6-pentamethylhept-3-ene was observed, with total turnovers of 44−78. Unfortunately, the lifetime of the catalyst at these temperatures limits the utility of the process; pseudo-first-order kinetic plots of ln[neohexene] versus time for the dimerization are linear over at least one half-life, but extended heating in bromobenzene-$d_5$ leads to slow decomposition of the catalyst and a concomitant decrease in the observed reaction rate over time. Activation parameters determined for the conversion of neohexene to (*E*)-2,2,5,6,6-pentamethylhept-3-ene over the temperature range 70−95 °C are $\Delta H^{\ddagger} = 13(2)$ kcal/mol and $\Delta S^{\ddagger} = -22(4)$ cal/mol·K. The negative value of $\Delta S^{\ddagger}$ calculated for the catalysis is characteristic of a highly ordered transition state and is consistent with our identification of $\sigma$-bond metathesis as the rate-determining step.

Although the activity and turnover numbers are low, the selectivity of this process is noteworthy and stems from the alternating insertion/$\sigma$-bond metathesis catalytic cycle. Such cycles are relatively rare. A few examples have been reported of neutral [$Cp^*_2LnR$] complexes reacting with 1-alkynes to give 2,4-disubstituted but-1-en-3-ynes through an alternating $\sigma$-bond/migratory insertion mechanism similar to that proposed here.[14a] In a related reaction involving a $d^0$ complex, Horton has reported the isolation of [$Cp^*_2Zr(CH{=}C\{R\}C{\equiv}CR)$]$^+$ (R = $^t$Bu, $^n$Pr) derived from the reaction of 1-alkynes with the cationic zirconocene [$Cp^*_2ZrMe$][$B(4\text{-}C_6H_4F)_4$].[29] This is analogous to the reaction of [$Cp^*Ti(NP^tBu_3)Me$][$B(C_6F_5)_4$] with neohexene to form **1**, in that both the Zr and Ti reactions involve initial 1,2-insertion of an unsaturated substrate into a M−C bond, followed by $\sigma$-bond metathesis and a second 1,2-insertion reaction.[30] The ability of these $d^0$ systems to alternate between $\sigma$-bond metathesis and insertion reactions is a measure of the steric bulk around the metal center, as less sterically encumbered metal complexes or less bulky substrates (with Zr) produce mixtures of oligomers. Isolation of species such as [$Cp^*_2Zr(CH{=}C\{R\}C{\equiv}CR)$]$^+$ (R = $^t$Bu, $^n$Pr) is significant, because this complex is a catalytically active intermediate for the selective dimerization of alkynes, suggesting that complex **1** could be active for catalytic dimerization of neohexene to (*E*)-2,2,5,6,6-pentamethylhept-3-ene under suitable conditions.[14b,c,31]

## Conclusions

In conclusion, the titanium-phosphinimide cation [$Cp^*Ti(NP^tBu_3)Me$][$B(C_6F_5)_4$] reacts with the bulky α-olefin neohexene via 1,2-insertion to give **4**, which then reacts with additional neohexene through sequential $\sigma$-bond metathesis/1,2-insertion reactions to give ion pair **1**. At elevated temperatures in the presence of excess neohexene, **1** reacts via alternating $\sigma$-bond metathesis/insertion to catalyze the dimerization of neohexene to (*E*)-2,2,5,6,6-pentamethylhept-3-ene, suggesting that the $\sigma$-bond metathesis/insertion sequence observed here is a viable method for production of functionalized organic compounds from sterically encumbered olefins. However, the general applicability of the proposed dimerization has not yet been investigated, and it is not clear whether [$Cp^*Ti(NP^tBu_3)Me$][$B(C_6F_5)_4$] can successfully dimerize olefins other than neohexene.

## Experimental Section

**General Considerations.** Unless otherwise noted, all reactions and manipulations were performed under argon in an MBraun 150 M glovebox or using conventional Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories and vacuum transferred from over sodium/benzophenone (benzene-$d_6$, bromobenzene-$d_5$, toluene-$d_8$) or calcium hydride (dichloromethane-$d_2$) before use. 3,3-Dimethylbut-1-ene (neohexene) was purchased from Aldrich Chemical Co. and vacuum transferred from over sodium before use. $Cp^*Ti(NP^tBu_3)Me_2$[7d] was prepared according to literature methods. [$Ph_3C$][$B(C_6F_5)_4$] was provided as a generous gift from NOVA Chemicals Corporation. NMR spectra were acquired on a Bruker DMX 300 operating at 300 MHz for $^1H$, 75 MHz for $^{13}C$, and 121 MHz for $^{31}P$; a Bruker AMX 300 operating at 282 for $^{19}F$; and a Bruker DRX 400 operating at 400 MHz for $^1H$, 100 MHz for $^{13}C$, 162 MHz for $^{31}P$, and 128 MHz for $^{11}B$. Chemical shifts are reported in ppm at 298 K unless otherwise stated. $^1H$ chemical shifts are referenced to residual protonated solvent peaks at 7.30 ($C_6HD_4Br$), 7.16 ($C_6HD_5$), and 5.32 ppm ($CHDCl_2$). $^{13}C$ chemical shifts are reported relative to tetramethylsilane, $^{31}P$ chemical shifts are reported relative to 85% $H_3PO_4$(aq), $^{19}F$ chemical shifts are reported relative to $C_6H_5F$, and $^{11}B$ chemical shifts are reported relative to $BF_3\cdot Et_2O$. Microanalysis was

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(28) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev* **2000**, *100*, 1253, and references therein. $\beta$-$CH_3$ elimination is quite facile in complexes with a bulky ligand set, such as that found here.

(29) Horton, A. D., Jr. *J. Chem. Soc., Chem. Commun.* **1992**, 185. Similar reactivity has been observed in the gas phase; see: Christ C. S., Jr.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 596.

(30) Addition of 3 equiv of $HC{\equiv}C^tBu$ to [$Cp^*Ti(NP^tBu_3)Me$][$B(C_6F_5)_4$] produces the directly analogous complex [$Cp^*Ti(NP^tBu_3)(CH{=}C\{^tBu\}C{\equiv}C^tBu)$][$B(C_6F_5)_4$], confirming the validity of this comparison.

(31) (a) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 643. (b) Sadow, A. D.; Tilley, T. D. *Organometallics* **2003**, *22*, 3577.

performed by Mr. Jian Jun (Johnson) Li in the Department of Chemistry, University of Calgary.

**Synthesis of [Cp*Ti(NP$^t$Bu$_3$)(C$_{12}$H$_{23}$)][B(C$_6$F$_5$)$_4$] (1).** In a 100 mL round-bottomed flask, Cp*Ti(NP$^t$Bu$_3$)Me$_2$ (1.00 g, 2.33 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (2.15 g, 2.33 mmol) were dissolved in 10 mL of chlorobenzene and stirred for 5 min to give a dark orange solution. Neohexene (1.2 mL, 9.3 mmol) was added to the orange solution, which immediately turned dark red. The mixture was stirred for 20 min, followed by addition of 25 mL of hexanes to separate the product as a dark red oil that solidified into a red solid upon vigorous stirring. After decanting the pale orange supernatant, the red solid was washed with 2 × 5 mL of hexanes and then recrystallized from chlorobenzene (45 mL)/pentane (35 mL) to give **1** as dark red crystals. Yield: 2.45 g (85%). Anal. Calcd for $C_{58}H_{65}BF_{20}NPTi$: C, 55.92; H, 5.26; N, 1.12. Found: C, 55.67; H, 5.48; N, 1.12. $^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_5$Br, $\delta$): 148.9 (dm, $^1J_{CF}$ = 245 Hz, C$_{ortho}$), 138.7 (dm, $^1J_{CF}$ = 248 Hz, C$_{para}$), 136.8 (dm, $^1J_{CF}$ = 251 Hz, C$_{meta}$), 124.2 (br m, C$_{ipso}$). $^{19}$F{$^1$H} NMR (282 MHz, C$_6$D$_5$Br, $\delta$): −133.3 (F$_{ortho}$), −163.5 (F$_{para}$), −167.2 (F$_{meta}$). $^{11}$B{$^1$H} NMR (128 MHz, C$_6$D$_5$Br, $\delta$): −16.5.

**For 1$_{\mathbf{major}}$.** $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 197 K, $\delta$): 6.30 (dd, $^3J_{H\gamma H\delta}$ = 16.0 Hz, $^3J_{H\gamma H\beta}$ = 12.0 Hz, 1H, H$_\gamma$), 6.09 (d, $^3J_{H\delta H\gamma}$ = 16.0 Hz, 1H, H$_\delta$), 3.51 (dd, $^2J_{H\alpha' H\alpha}$ = 10.0 Hz, $^3J_{H\alpha' H\beta}$ = 13.6 Hz, 1H, H$_{\alpha'}$), 2.22 (br dd, $^2J_{H\alpha H\alpha'}$ = 10.0 Hz,$^3J_{H\alpha H\beta}$ = 7 Hz, 1H, H$_\alpha$), 2.00 (s, 15H, Cp*), 1.44 (d, $^3J_{HP}$ = 13.2 Hz, 27H, P$^t$Bu$_3$), 0.96 (s, 9H, C$_\delta$$^t$Bu), 0.81 (s, 9H, C$_\beta$$^t$Bu), 0.74 (ddd, $^3J_{H\beta H\alpha'}$ = 13.6 Hz, $^3J_{H\beta H\gamma}$ = 12.0 Hz, $^3J_{H\beta H\alpha}$ = 7 Hz, 1H, H$_\beta$). $^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$, 197 K, $\delta$): 157.1 (C$_\delta$), 134.6 (C$_\gamma$), 125.2 (C$_5${CH$_3$}$_5$), 82.3 (C$_\alpha$), 44.2 (C$_\beta$), 41.3 (d, $^1J_{CP}$ = 42 Hz, PC{CH$_3$}$_3$), 36.3 and 35.4 (C$_\beta$C{CH$_3$}$_3$ and C$_\delta$C{CH$_3$}$_3$), 30.7 (br, PC{CH$_3$}$_3$), 29.4 (C$_\delta$C{CH$_3$}$_3$), 28.0 (C$_\beta$C{CH$_3$}$_3$), 13.2 (C$_5${CH$_3$}$_5$). $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 197 K, $\delta$): 52.4.

**For 1$_{\mathbf{minor}}$.** $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 197 K, $\delta$): 7.57 (d, $^3J_{H\delta H\gamma}$ = 16.8 Hz, 1H, *H*$_\delta$), 5.33 (dd, $^3J_{H\gamma H\delta}$ = 16.8 Hz, $^3J_{H\gamma H\beta}$ = 12.4 Hz, 1H, *H*$_\gamma$), 3.10 (dd, $^2J_{H\alpha' H\alpha}$ = 11.2 Hz, $^3J_{H\alpha' H\beta}$ = 11.2 Hz, 1H, *H*$_{\alpha'}$), 2.66 (dd, $^2J_{H\alpha H\alpha'}$ = 11.2 Hz, $^3J_{H\alpha H\beta}$ = 6.4 Hz, 1H, *H*$_\alpha$), 2.30 (ddd, $^3J_{H\beta H\alpha'}$ = 11.2 Hz, $^3J_{H\beta H\gamma}$ = 12.4 Hz, $^3J_{H\beta H\alpha}$ = 6.4 Hz, 1H, *H*$_\beta$), 2.00 (s, 15H, *Cp**), 1.44 (d, $^3J_{HP}$ = 13.2 Hz, 27H, P*$^t$Bu$_3$*), 0.96 (s, 9H, C$_\delta$*$^t$Bu*), 0.81 (s, 9H, C$_\beta$*$^t$Bu*). $^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$, 197 K, $\delta$): 160.5 (*C*$_\delta$), 132.1 (*C*$_\gamma$), 128.4 (*C*$_5${CH$_3$}$_5$), 87.8 (*C*$_\alpha$), 42.1 (*C*$_\beta$), 41.3 (d, $^1J_{CP}$ = 42 Hz, P*C*{CH$_3$}$_3$), 36.3 and 35.4 (C$_\beta$*C*{CH$_3$}$_3$ and C$_\delta$*C*{CH$_3$}$_3$), 30.7 (br, PC{*C*H$_3$}$_3$), 29.4 (C$_\delta$C{*C*H$_3$}$_3$), 28.0 (C$_\beta$C{*C*H$_3$}$_3$), 13.2 (C$_5${*C*H$_3$}$_5$). $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 197 K, $\delta$): 52.6.

$^1J_{CH}$ values for **1** measured at 25 °C: $^1J_{CH\alpha}$ = 135 Hz; $^1J_{CHa'}$ = 138 Hz; $^1J_{CH\beta}$ = 131 Hz; $^1J_{CH\gamma}$ = 148 Hz; $^1J_{CH\delta}$ = 146 Hz.

**Methanolysis of [Cp*Ti(NP$^t$Bu$_3$)(C$_{12}$H$_{23}$)][B(C$_6$F$_5$)$_4$] (1).** Acidic methanol (1 M HCl in MeOH, 10 $\mu$L) was injected into a red solution of **2** (43 mg, $3.5 \times 10^{-5}$ mol) in 0.6 mL of bromobenzene-*d*$_5$, which immediately turned bright yellow. The yellow solution was passed through a 5 cm column of silica gel in a Pasteur pipet with additional bromobenzene-*d*$_5$ until approximately 0.7 mL was collected. The resulting pale yellow solution was analyzed by NMR spectroscopy and determined to contain (*E*)-2,2,5,6,6-pentamethylhept-3-ene. $^1$H NMR (300 MHz, C$_6$D$_5$Br, $\delta$): 5.40 (d, $^3J_{HH}$ = 15.6 Hz, 1H, C=C*H*$^t$Bu), 5.28 (dd, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 8.5 Hz, 1H, C*H*=CH$^t$Bu), 1.81 (dq, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*$^t$BuMe), 1.00 (s, 9H, C=C*$^t$Bu*), 0.92 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH$^t$Bu*Me*), 0.84 (s, 9H, CH*$^t$Bu*Me). $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_5$Br, $\delta$): 141.0 (C=*C*H$^t$Bu), 127.8 (*C*=CH$^t$Bu), 47.0 (*C*H$^t$BuMe), 32.6 (CHMe{*C*(CH$_3$)$_3$}), 32.5 (C=CH{*C*(CH$_3$)$_3$}), 29.8 (C=CH{C(*C*H$_3$)$_3$}), 27.4 (CHMe{C(*C*H$_3$)$_3$}), 15.8 (CH{*C*H$_3$}$^t$Bu).

**Synthesis of [Cp*Ti(NP$^t$Bu$_3$)(C$_{12}$H$_{23}$)(THF)][B(C$_6$F$_5$)$_4$] (2).** Complex **1** (54 mg, $4.3 \times 10^{-5}$ mol) was dissolved in 0.6 mL of CD$_2$Cl$_2$ in a 5 mm NMR tube sealed with a rubber septum, giving a red solution. The NMR sample was cooled in a dry ice/acetone bath, and dry THF (10 $\mu$L, $1.4 \times 10^{-4}$ mol) was injected into the sample by syringe; the tube was then removed from the cold bath and shaken well before being replaced in the cold bath; the solution turned bright orange upon mixing. The NMR tube was placed in an NMR probe precooled to –50 °C. Conversion of **1** to **2** was quantitative by $^1$H NMR spectroscopy. Attempts to isolate **2** gave sticky oils; a single crystal suitable for X-ray crystallographic analysis was eventually grown from a dilute solution of CD$_2$Cl$_2$/hexanes at −35 °C.

**Major Diastereomer (60%).** $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 220 K, $\delta$): 5.27 (d, $^3J_{H\delta H\gamma}$ = 15.6 Hz, 1H, *H*$_\delta$), 4.84 (dd, $^3J_{H\gamma H\delta}$ = 15.6 Hz, $^3J_{H\gamma H\beta}$ = 10.0 Hz, 1H, *H*$_\gamma$), 4.02 (br m, 2H, Ti-OC*H*$_2$), 3.79 (br m, 2H Ti-OC*H*$_2$), 3.68 (m, 1H, *H*$_{\alpha'}$), 3.03 (m, 1H, *H*$_\beta$), 2.09 (br m, 2H, Ti-OCH$_2$C*H*$_2$), 2.02 (s, 15H, *Cp**), 1.95 (br m, 2H, Ti-OCH$_2$C*H*$_2$), 1.44 (d, $^3J_{HP}$ = 13.6 Hz, 27H, P*$^t$Bu$_3$*), 0.89 (s, 9H, C$_\delta$*$^t$Bu*), 0.70 (s, 9H, C$_\beta$*$^t$Bu*), −0.61 (dd, $^2J_{H\alpha H\alpha'}$ = 5.2 Hz,$^3J_{H\alpha H\beta}$ = 1.9 Hz, 1H, *H*$_\alpha$). $^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$, 220 K, $\delta$): 143.1 (*C*$_\delta$), 124.8 (*C*$_\gamma$), 124.1 (*C*$_5${CH$_3$}$_5$), 98.6 (*C*$_\alpha$), 75.2 (Ti-O*C*H$_2$), 59.3 (*C*$_\beta$), 41.3 (d, $^1J_{CP}$ = 44 Hz, P*C*{CH$_3$}$_3$), 36.5 and 33.2 (C$_\beta$*C*{CH$_3$}$_3$ and C$_\delta$*C*{CH$_3$}$_3$), 30.7 (br, PC{*C*H$_3$}$_3$), 29.2 (C$_\beta${C(*C*H$_3$)$_3$}), 27.5 (C$_\delta${C(*C*H$_3$)$_3$}), 26.4 (Ti-OCH$_2$*C*H$_2$), 12.5 (C$_5${*C*H$_3$}$_5$). $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 220 K, $\delta$): 48.8.

**Minor Diastereomer (40%).** $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 220 K, $\delta$): 5.36 (d, $^3J_{H\delta H\gamma}$ = 16.0 Hz, 1H, *H*$_\delta$), 4.65 (dd, $^3J_{H\gamma H\delta}$ = 15.6 Hz, $^3J_{H\gamma H\beta}$ = 9.2 Hz, 1H, *H*$_\gamma$), 4.02 (br m, 2H, Ti-OC*H*$_2$), 3.79 (br m, 2H Ti-OC*H*$_2$), 2.98 (m, 1H, *H*$_\beta$), 2.88 (m, 1H, *H*$_{\alpha'}$), 2.09 (br m, 2H, Ti-OCH$_2$C*H*$_2$), 2.04 (s, 15H, *Cp**), 1.95 (br m, 2H, Ti-OCH$_2$C*H*$_2$), 1.46 (d, $^3J_{HP}$ = 13.2 Hz, 27H, P*$^t$Bu$_3$*), 0.89 (s, 9H, C$_\delta$*$^t$Bu*), 0.65 (s, 9H, C$_\beta$*$^t$Bu*), 0.54 (d, $^2J_{H\alpha H\alpha'}$ = 11.2 Hz, 1H, *H*$_\alpha$). $^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$, 220 K, $\delta$): 141.8 (*C*$_\delta$), 128.2 (*C*$_\gamma$), 124.7 (*C*$_5${CH$_3$}$_5$), 88.5 (*C*$_\alpha$), 77.3 (Ti-O*C*H$_2$), 55.9 (*C*$_\beta$), 41.2 (d, $^1J_{CP}$ = 45 Hz, P*C*{CH$_3$}$_3$), 36.0 and 33.2 (C$_\beta$*C*{CH$_3$}$_3$ and C$_\delta$*C*{CH$_3$}$_3$), 30.7 (br, PC{*C*H$_3$}$_3$), 29.1 (C$_\beta${C(*C*H$_3$)$_3$}), 27.3 (C$_\delta${C(*C*H$_3$)$_3$}), 25.4 (Ti-OCH$_2$*C*H$_2$), 12.5 (C$_5${*C*H$_3$}$_5$). $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 220 K, $\delta$): 49.0.

**Synthesis of Cp*Ti(NP$^t$Bu$_3$)(C$_{12}$H$_{23}$)Cl (3).** In a 50 mL round bottomed flask, *n*Bu$_4$NCl (47 mg, 0.17 mmol) and **1** (201 mg, 0.161 mmol) were dissolved in 25 mL of dichloromethane to give a bright yellow solution that was stirred at 20 °C for 30 min. The solvent was then removed under vacuum to give a pale yellow foam, which was sonicated with 25 mL of hexanes, followed by filtration to remove a white precipitate. Solvent was removed from the filtrate under vacuum to give **3** as a bright yellow powder. Yield: 75 mg (77%). Anal. Calcd for $C_{34}H_{65}ClNPTi$: C, 67.81; H, 10.88; N, 2.33. Found: C, 68.00; H, 10.84; N, 2.65.

**Major Diastereomer (85%).** $^1$H NMR (300 MHz, C$_6$D$_6$, $\delta$): 5.36 (d, $^3J_{H\delta H\gamma}$ = 15.9 Hz, $^1J_{CH\delta}$ = 145 Hz, 1H, *H*$_\delta$), 5.17 (dd, $^3J_{H\gamma H\delta}$ = 15.9 Hz, $^3J_{H\gamma H\beta}$ = 9.6 Hz, $^1J_{CH\gamma}$ = 148 Hz, 1H, *H*$_\gamma$), 3.14 (dd, $^2J_{H\alpha' H\alpha}$ = 12.0 Hz, $^3J_{H\alpha' H\beta}$ = 12.0 Hz, $^1J_{CH\alpha'}$ = 117 Hz, 1H, *H*$_{\alpha'}$), 2.55 (ddd, $^3J_{H\beta H\alpha'}$ = 12.0 Hz, $^3J_{H\beta H\gamma}$ = 9.6 Hz, $^3J_{H\beta H\alpha}$ = 2.2 Hz, $^1J_{CH\beta}$ = 125 Hz, 1H, *H*$_\beta$), 2.14 (s, 15H, *Cp**), 1.30 (d, $^3J_{HP}$ = 13.0 Hz, 27H, P*$^t$Bu$_3$*), 1.27 (s, 9H, C$_\delta$*$^t$Bu*), 1.08 (s, 9H, C$_\beta$*$^t$Bu*), 0.37 (dd, $^2J_{H\alpha H\alpha'}$ = 12.0 Hz,$^3J_{H\alpha H\beta}$ = 2.2 Hz, $^1J_{CH\alpha}$ = 117 Hz 1H, *H*$_\alpha$). $^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_6$, $\delta$): 140.0 (*C*$_\delta$), 130.4 (*C*$_\gamma$), 121.3 (*C*$_5${CH$_3$}$_5$), 68.4 (*C*$_\alpha$), 54.0 (*C*$_\beta$), 42.3 (d, $^1J_{CP}$ = 45 Hz, P*C*{CH$_3$}$_3$), 36.3 and 33.9 (C$_\beta$*C*{CH$_3$}$_3$ and C$_\delta$*C*{CH$_3$}$_3$), 30.5 (C$_\beta${*C*(CH$_3$)$_3$}), 30.4 (PC{*C*H$_3$}$_3$)), 28.9 (C$_\delta${*C*(CH$_3$)$_3$}), 13.3 (C$_5${*C*H$_3$}$_5$). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_5$Br, $\delta$): 37.3.

**Minor Diastereomer (15%).** $^1$H NMR (300 MHz, C$_6$D$_6$, $\delta$): 5.42 (d, $^3J_{H\delta H\gamma}$ = 15.9 Hz, 1H, *H*$_\delta$), 5.09 (dd, $^3J_{H\gamma H\delta}$ = 15.9 Hz, $^3J_{H\gamma H\beta}$ = 9.3 Hz, 1H, *H*$_\gamma$), 2.60 (dm, $^3J_{H\beta H\gamma}$ = 9.3 Hz, 1H, *H*$_\beta$), 2.11 (s, 15H, *Cp**), 1.30 (d, $^3J_{HP}$ = 13.0 Hz, 27H, P*$^t$Bu$_3$*), 1.61 (m, 1H, *H*$_\alpha$), 1.32 (m, 1H, *H*$_\alpha$), 1.24 (s, 9H, C$_\delta$*$^t$Bu*), 1.10 (s, 9H, C$_\beta$*$^t$Bu*). $^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_6$, $\delta$): 141.4 (*C*$_\delta$), 129.5 (*C*$_\gamma$), 121.5 (*C*$_5${CH$_3$}$_5$), 68.4 (*C*$_\alpha$), 56.3 (*C*$_\beta$), 41.9 (d, $^1J_{CP}$ = 45 Hz, P*C*{CH$_3$}$_3$), 36.8 and 33.7 (C$_\beta$*C*{CH$_3$}$_3$ and C$_\delta$*C*{CH$_3$}$_3$), 30.6 (C$_\beta${*C*(CH$_3$)$_3$}),

30.2 (PC{*C*H$_3$}$_3$)), 29.0 (C$_\delta${*C*(CH$_3$)$_3$}), 13.5 (C$_5${*C*H$_3$}$_5$). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_5$Br, $\delta$): 38.0.

**Synthesis of [Cp*Ti(NP$^t$Bu$_3$)(CH$_2$CH{Me}$^t$Bu)][B(C$_6$F$_5$)$_4$] (4).** In an NMR tube, Cp*Ti(NP$^t$Bu$_3$)Me$_2$ (33 mg, $7.7 \times 10^{-5}$ mol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (72 mg, $7.8 \times 10^{-5}$ mol) were dissolved in 0.7 mL of dichloromethane-$d_2$. The tube was sealed with a septum, and the sample cooled to −80 °C in a dry ice/acetone bath. When the sample was cold, neohexene (10 $\mu$L, $7.8 \times 10^{-5}$ mol) was injected into the NMR tube via syringe, and the sample quickly shaken before placing back in the cold bath. The sample was placed in the NMR probe, which was precooled to −20 °C; after 5 min at −20 °C the majority of the sample had converted to compound **4**. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 250 K, $\delta$): 3.79 (dd, $^2J_{\mathrm{H\alpha'H\alpha}} = 8.5$ Hz, $^3J_{\mathrm{H\alpha H\beta}} = 11.1$ Hz, 1H, $H_{\alpha'}$), 2.73 (ddq, $^2J_{\mathrm{H\beta H\alpha}} = 11.1$ Hz, $^3J_{\mathrm{H\beta H\alpha'}} = 4.4$ Hz, $^3J_{\mathrm{H\beta H}} = 6.8$ Hz, 1H, $H_\beta$), 2.09 (s, 15H, *Cp**), 1.52 (d, $^3J_{\mathrm{HP}} = 13.6$ Hz, 27H, P$^t$*Bu$_3$*), 0.80 (s, 9H, $^t$*Bu*), 0.61 (d, $^3J_{\mathrm{HH\beta}} = 6.8$ Hz, 3H, C$_\beta$*Me*), 0.07 (dd, $^2J_{\mathrm{H\alpha H\alpha'}} = 8.5$ Hz, $^3J_{\mathrm{H\alpha H\beta}} = 4.4$ Hz, 1H, $H_\alpha$). $^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$, 200 K, $\delta$): 126.4 (*C$_5$*{CH$_3$}$_5$), 109.5 (Ti*C*H$_2$), 50.8 (*C$_\beta$*CH$_3$), 41.4 (d, $^1J_{\mathrm{CP}} = 42$ Hz, P*C*{CH$_3$}$_3$), 33.7 (C$_\beta$*C*{CH$_3$}$_3$), 30.4 (PC{*C*H$_3$}$_3$), 26.1 (C$_\beta$C{*C*H$_3$}$_3$), 17.7 (C$_\beta$*C*H$_3$), 12.5 (C$_5${*C*H$_3$}$_5$). $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 250 K, $\delta$): 54.7.

**Line-Shape Analysis of 1 and Related Calculations.** Line-shape analysis was carried out on the olefin (8.0−4.0 ppm) and Ti-CH$_2$ (3.5−2.0 ppm) regions of $^1$H NMR spectra (400 MHz) recorded for compound **1** in dichloromethane-$d_2$/bromobenzene-$d_5$ at 185−355 K using a modified version of DNMR3[32] contained in SpinWorks 2.4.[33] Rate constants ($k$) were determined iteratively at each temperature for the two-site exchange (site population 19:1) to give a good match between calculated and experimental spectra. Estimated errors in $k$ varied from 2 to 10%, temperatures are ±3 K. Thermodynamic parameters were obtained from the slope and intercept of an Eyring plot ($\ln(k/T)$ vs $1/T$); values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are reported in the text.

**Kinetic Measurements for Dimerization of Neohexene by [Cp*Ti(NP$^t$Bu$_3$)(C$_{12}$H$_{23}$)][B(C$_6$F$_5$)$_4$] (1).** Compound **1**, bromobenzene-$d_5$, and neohexene were loaded into a 5 mm NMR tube sealed with a rubber septum ($V_{\mathrm{tot}} = 0.70$ mL). The sample was heated in the NMR probe and the reaction followed by $^1$H NMR spectroscopy, monitoring the integrated intensity of the neohexene H$_\gamma$ olefin signal against product olefin resonances. Plots of ln[neohexene] versus time were linear over 1−2 half-lives with excess neohexene; only data from the first half-life were considered. Values obtained for $k$ at 368, 360, 354, and 345 K ([neohexene] = 1.1 M, [**1**] = 14 mM) were used to construct an Eyring plot ($R^2 = 0.972$); thermodynamic parameters were obtained from the slope and intercept of this plot and are reported in the text.

**Determination of Kinetic Isotope Effect for Formation of 1.** A stock solution containing (*E*)-1-*D*-neohexene (0.27 M) and (*Z*)-1-*D*-neohexene (0.30 M) was prepared in dichloromethane-$d_2$ (concentration checked by integration against a known amount of 1,3,5-trimethoxybenzene). Cp*Ti(NP$^t$Bu$_3$)Me$_2$ (10 mg, $2.3 \times 10^{-5}$ mol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (21 mg, $2.3 \times 10^{-5}$ mol) were dissolved in 0.3 mL of dichloromethane-$d_2$ in an NMR tube sealed with a rubber septum to generate [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$] ($2.3 \times 10^{-5}$ mol) as an orange solution. The NMR tube was cooled to −78 °C in a dry ice/acetone bath, and 0.40 mL of neohexene stock solution was injected into the NMR tube by syringe. Once the contents of the NMR tube had cooled to −78 °C, the sample was mixed by shaking rapidly and immediately placed into an ice bath at 0 °C for 4.5 h until formation of **1** was complete. The NMR sample was then warmed to 20 °C and a $^1$H NMR spectrum acquired; integration of the olefin peaks in **1** was used to calculate the KIE: $k_{\mathrm{H}}/k_{\mathrm{D}} = 3.0 \pm 0.3$.

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**Supporting Information Available:** Crystallographic data for compounds **1**, **2**, and **3**, including tables of crystal data and ORTEP diagrams, and crystallographic information files (CIF). $^1$H NMR spectra for reaction of [Cp*Ti(NP$^t$Bu$_3$)Me][B(C$_6$F$_5$)$_4$] with (*E*)-1-*d*-neohexene and $^1$H and $^{13}$C NMR spectra for compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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