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Kinetics and Mechanism of Formation of Yttrium Alkyl Complexes from $(Cp^*{}_2YH)_2$ and Alkenes

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The dissociation of the dimer $(Cp^*{}_2YH)_2$ (**2**) to the $Cp^*{}_2YH$ monomer is an important process in reactions of **2** with alkenes. The rate of dissociation of **2** was measured by NMR line-broadening techniques (14 s^{-1} at 0 °C, $\Delta G^{\ddagger} = 14.5$ kcal mol^{-1}, $\Delta H^{\ddagger} = 14.9(8)$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 3(2)$ eu). A full range of dissociative and associative mechanisms for reaction of alkenes with **2** was found. For the most crowded and least reactive alkenes studied, 2-butene and 2-methylpropene, reaction with **2** occurred slower than dissociation of dimer **2**; kinetic studies established reversible dissociation of **2** to monomeric $Cp^*{}_2YH$ followed by competitive trapping by alkene and recombination to regenerate **2**. Kinetic studies of the less crowded alkene 3-methyl-1-butene are consistent with rate-limiting dissociation of dimer **2** followed by efficient trapping of the intermediate $Cp^*{}_2YH$ by alkene. The least crowded terminal alkenes such as 1-hexene reacted with **2** at a rate faster than dimer dissociation; kinetic studies established a two-component rate law involving a second-order term for direct attack of alkene on the dimer and a first-order term involving rate-determining dimer dissociation followed by rapid alkene reaction with monomeric $Cp^*{}_2YH$. The reactions of terminal alkenes with **2** initially gave mixtures of single- and double-alkene-insertion products but no triple-insertion products. The initially formed *n*-alkyl yttrium complex reacts with terminal alkenes at a rate similar to the reaction of yttrium hydride dimer **2** with terminal alkenes. The more crowded β-alkyl yttrium double-insertion product is much less reactive toward terminal alkenes.

Introduction

The insertion of an alkene into lanthanide and group 3 hydride bonds represents an important elementary step in catalysis of alkene hydrogenation[1] and hydrosilylation.[2] Furthermore, the reaction of alkenes with d^0 metal−hydride bonds is important in the initiation and chain transfer steps of alkene oligomerization and polymerization.[3−5] Bis(cyclopentadienyl)yttrium hydrides have been shown to be among the most active ethylene polymerization catalysts, and recently Bercaw has designed **1** for the isospecific polymerization of propene (Scheme 1).[5] Alkene polymerization by lanthanide hydrides and alkyls has received much attention because the catalysts are active and can be studied without the need for a cocatalyst. This provides the basis for the “lanthanide model”[6] of Ziegler−Natta olefin polymerization.

We have investigated d^0 yttrium[7] and zirconium[8] metal alkyl−alkene complexes as models of Ziegler−Natta polymerization intermediates. Given the results of these studies, we were interested in preparing monomeric yttrium alkyl complexes for the study of *non-chelated* yttrium alkyl−alkene complexes.[7e] In addition to the synthesis of bis(pentamethylcyclopentadienyl)-

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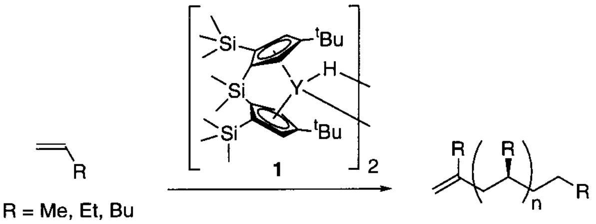
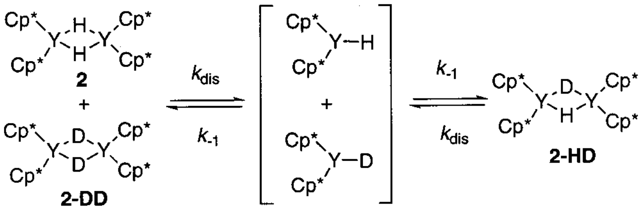
Scheme 1



Scheme 2



yttrium alkyl complexes, a kinetic study of the reaction of yttrium hydrides with alkenes was undertaken. Here we present the results of a mechanistic study of the reaction of $(\mathrm{Cp^*_2YH})_2$ (**2**)[9] with alkenes. We report that reaction of **2** with alkenes occurs by three distinct mechanisms, depending on the substitution of the alkene.

Results

Kinetics of Approach to Equilibrium: $(\mathrm{Cp^*_2YH})_2$ + $(\mathrm{Cp^*_2YD})_2$. It has been suggested that dissociation of $(\mathrm{Cp^*_2LnH})_2$ to the reactive monomer, $\mathrm{Cp^*_2LnH}$, is the first step in the reaction of $(\mathrm{Cp^*_2LnH})_2$ with alkenes.[3] Prior to studying the reactions of alkenes with $(\mathrm{Cp^*_2YH})_2$ (**2**), it is important to know the rate of dissociation of **2** to monomeric $\mathrm{Cp^*_2YH}$ in order to determine whether dissociation is rapid enough to be a kinetically competent step in the reactions with alkenes.

2 was prepared by the hydrogenation of $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ in methylcyclohexane-d_{14}. at 0 °C.[9] The ^{1}H NMR spectrum of **2** at −40 °C exhibits a triplet at δ 5.35 due to coupling to ^{89}Y (100%, $I = 1/2$). When **2** was mixed with a solution of $(\mathrm{Cp^*_2YD})_2$ (**2-DD**) at −78 °C, an additional triplet appeared at δ 5.33, which we attribute to the bridging hydride of $\mathrm{Cp^*_2Y_2}(\mu\text{-H})(\mu\text{-D})$ (**2-HD**) (Scheme 2).

The rate of approach to equilibrium of **2** and **2-DD** was determined by first mixing solutions at −100 °C and then warming the solution to −85 °C in the NMR probe and watching the growth of **2-HD**. Although it was difficult to accurately determine the exchange rate using this method, we were able to estimate that the rate of approach to equilibrium is about 1×10^{-3} s^{-1} at − 85 °C ($t_{1/2} \approx 10$ min). From this value, we estimate that the rate of dimer dissociation is 3×10^{-4} s^{-1} ($\Delta G^\ddagger \approx 14$ kcal mol^{-1}).

A more accurate method of determining the rate of dissociation of **2** involves observation of the temperature dependence of the hydride resonance. Below −40 °C, the hydride resonance is a triplet coupled to two equivalent ^{89}Y atoms. When the temperature is raised, the hydride resonance shifts and broadens (Figure 1). We attribute the broadening to an increasing rate of dissociation, resulting in loss of coupling between the hydride and one of the ^{89}Y nuclei. Analysis of the line broadening gave a rate of dissociation of dimer **2** at 0 °C of 14 s^{-1} ($t_{1/2}$ = 49 ms). Activation parameters, $\Delta G^\ddagger = 14.5$ kcal mol^{-1}, $\Delta H^\ddagger = 14.9(8)$ kcal mol^{-1}, and $\Delta S^\ddagger = 3(2)$ eu, were obtained from an Eyring analysis of the line broadening data at various temperatures (Figure 2).[10] These parameters allow extrapolation to the lower temperatures, where reaction of **2** with alkenes can be conveniently measured.

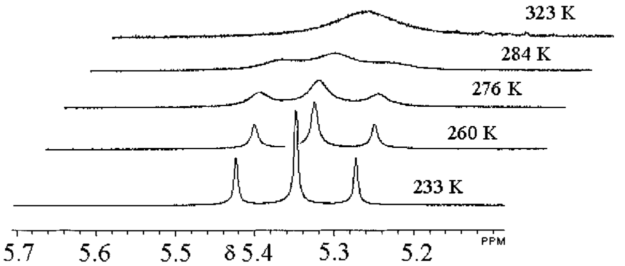


Figure 1. Line broadening of the hydride resonance of $(\mathrm{Cp^*_2YH})_2$ (**2**) in the absence of $\mathrm{H_2}$.

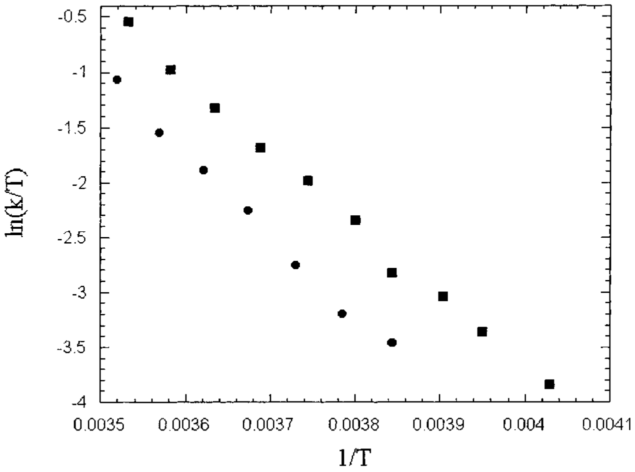


Figure 2. Eyring plot of the observed rate of loss of Y−H coupling: (■) in the absence of $\mathrm{H_2}$; (●) in the presence of 3−4 atm of $\mathrm{H_2}$.

A similar experiment was done in which the line broadening of **2** was monitored in the presence of ~3 atm of $\mathrm{H_2}$. At −60 °C, **2** and $\mathrm{H_2}$ exhibited sharp resonances at δ 5.34 and 4.53 ppm, respectively, indicating that exchange is slow on the NMR time scale. Warming this sample above −30 °C resulted in broadening of both the bridging hydride and the $\mathrm{H_2}$ resonances. Interestingly, similar broadening of the yttrium hydride triplet in the presence of $\mathrm{H_2}$ occurred at approximately 10 °C lower temperature than in the absence of $\mathrm{H_2}$. Comparison of the two rates at −13 °C shows that the rate of the process giving rise to loss of coupling is 1.8 times faster in the presence of $\mathrm{H_2}$ than in its absence.

Bercaw has noted that monomeric $\mathrm{Cp^*_2ScH}$ undergoes fast exchange with $\mathrm{H_2}$, even at −95 °C.[11] If we assume that monomeric $\mathrm{Cp^*_2YH}$ behaves similarly and

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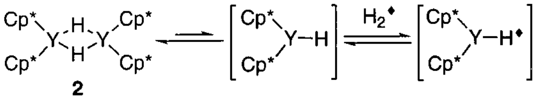
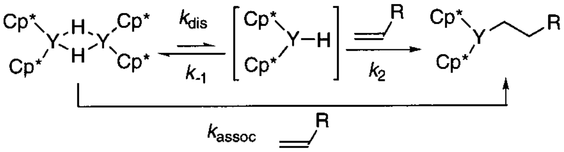
Scheme 3



Scheme 4



exchanges rapidly with H_2, then each dissociation of $(Cp^*_2YH)_2$ (**2**) will result in complete loss of Y−H coupling due to exchange with H_2. However, in the absence of H_2, dissociation produces Cp^*_2YH, which has a 50:50 chance of recombining with an yttrium to form the same spin state from which it came.[10b] Under this assumption, the resulting rate of coupling loss in the absence of H_2 will be half the rate observed in the presence of H_2. This model is consistent with the observed rate ratio of 1.8. Correcting for this statistical factor of 2, the rate of dimer dissociation remains unchanged in the presence of H_2.

Although an associative exchange with hydrogen remains possible, the similarity of the activation parameters after statistical correction and the small value of $\Delta S^{\ddagger}$ indicate that the loss of Y−H coupling occurs through the same dissociative mechanism whether H_2 is present or not (Scheme 3).

Insertion of Alkenes into Yttrium−Hydride Bonds. A priori, there are several different kinetic mechanisms that can be considered for the reaction of alkenes with $(Cp^*_2YH)_2$ (**2**) that fall into two classes: associative and dissociative mechanisms (Scheme 4). Attack of the alkene on dimer **2** is the first step in associative mechanisms and would have a rate law first order in [**2**] and first order in [alkene] (eq 1). There are

Associative Mechanisms

$$-\frac{d[\mathbf{2}]}{dt} = k_{assoc}[\mathbf{2}][\text{alkene}] \qquad (1)$$

Dissociative Mechanisms

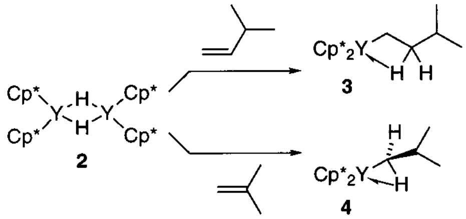
$$\text{if } k_2[\text{alkene}] \gg k_{-1}[\text{Cp}^*{}_2\text{YH}] \qquad -\frac{d[\mathbf{2}]}{dt} = k_{dis}[\mathbf{2}] \qquad (2)$$

$$\text{if } k_2[\text{alkene}] \ll k_{-1}[\text{Cp}^*{}_2\text{YH}]$$

$$-\frac{d[\mathbf{2}]}{dt} = k_2 K_{eq}{}^{1/2}[\mathbf{2}]^{1/2}[\text{alkene}] \qquad (3)$$

three kinetic variations on dissociative mechanisms that begin with dissociation of dimer **2** to the more reactive monomer Cp^*_2YH. If dissociation of **2** is the rate-determining step and the monomer Cp^*_2YH is rapidly trapped by alkene, then the reaction kinetics would be first order in [**2**] and zero order in [alkene] (eq 2). At the other end of the kinetic spectrum, if dissociation of dimer **2** is fast and reversible and reaction of monomer Cp^*_2YH with the alkene is rate determining, then the reaction kinetics would be half-order in [**2**] and first order in [alkene] (eq 3). If the monomer Cp^*_2YH recombines to regenerate **2** at a rate comparable to its reaction with an alkene, then very complex kinetics will be observed between half order and first order in [**2**] and between first order and zero order in [alkene]. It is interesting that, in the course of studying a relatively small range of alkenes, we have encountered all of these kinetic mechanisms.

Scheme 5



Reaction with 3-Methyl-1-butene: Rate-Determining Dissociation of 2. Reaction of $(Cp^*_2YH)_2$ (**2**) with 3-methyl-1-butene occurred rapidly at −50 °C to produce $Cp^*_2YCH_2CH_2CH(CH_3)_2$ (**3**) in quantitative NMR yield ($(CH_2(SiMe_3)_2$ internal standard) (Scheme 5). Only a single alkene inserts up to −30 °C, where slow decomposition begins. Due to its high air and temperature sensitivity, the yttrium alkyl complex was characterized in situ using a combination of ^1H, ^{13}C, COSY, HMQC, and TOCSY NMR spectroscopy. The YCH_2 group gives rise to a broad ^1H NMR resonance at δ 0.27 coupled to both Y and a neighboring methylene group and in the ^{13}C NMR spectrum to a triplet of doublets (J_{CH} = 124 Hz, $^1J_{YC}$ = 36 Hz) at δ 38.9. Coupling to a single Y rules out bridging alkyl groups and establishes the monomeric nature of yttrium alkyl **3**. The β-methylene $YCH_2\mathit{CH_2}$ group gives rise to a high-frequency ^1H NMR resonance at δ −0.12 and to a ^{13}C NMR resonance at δ 46.7 with a small J_{CH} = 108 Hz that provide evidence for a β-agostic interaction.

The kinetics of the reaction of dimer **2** (0.01 M) with 3-methyl-1-butene were monitored under pseudo-first-order conditions of a >10-fold excess of alkene. Reaction of 3-methyl-1-butene with yttrium hydride dimer **2** was found to be first-order in **2**, as was evident from linear $\ln[\mathbf{2}_0]/[\mathbf{2}_t]$ vs t plots. Variation of the alkene concentration showed that the insertion is zero-order in alkene. For example, the rate of 3-methyl-1-butene insertion at −80 °C was invariant at $[2.2(2)] \times 10^{-4}$ s^{-1} ($t_{1/2}$ = 52 min) between 0.2 and 0.5 M alkene. The observed rate law (eq 2) is consistent with a mechanism involving rate-determining dissociation of $(Cp^*_2YH)_2$ (**2**) followed by rapid alkene insertion into the monomeric Cp^*_2YH.

This mechanism requires that the rate of dissociation of dimer **2** independently measured by NMR line broadening be the same as the rate of dimer reaction with 3-methyl-1-butene. It is difficult to extrapolate from NMR rates measured between −20 and 20 °C to alkene insertion rates measured between −75 and −90 °C. Extrapolation of NMR rates to −80 °C gives a rate of dimer dissociation of $[4(4)] \times 10^{-4}$ s^{-1}, which is in moderate agreement with the rate constant (2.2×10^{-4} s^{-1}) for disappearance of **2** in the reaction with 3-methyl-1-butene**.** Perhaps a better comparison is to see if rate constants for dimer dissociation measured by NMR

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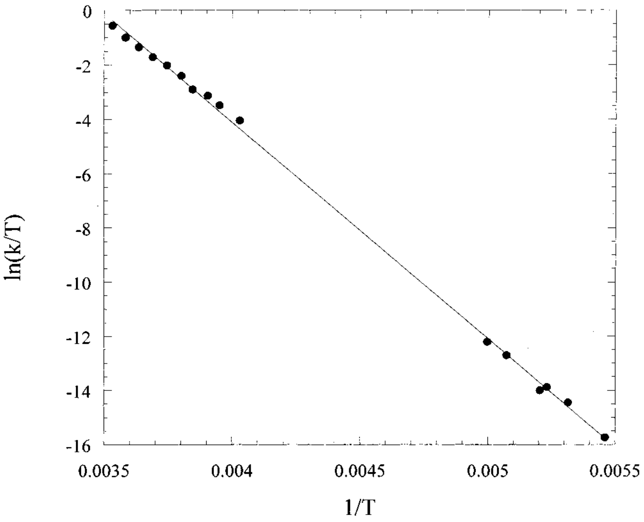


Figure 3. Eyring plot of combined NMR line broadening and 3-methyl-1-butene insertion determinations of k_{dis}, the rate constant for dissociation of dimer **2**.

broadening and by rapid trapping with 3-methyl-1-butene fall on the same line. Figure 3 shows a remarkable correlation between rates determined over a 110 °C range ($\Delta H^{\ddagger} = 15.8(2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6(1)$ eu). These data provide further support for rate-determining dissociation of **2** followed by rapid insertion of 3-methyl-1-butene into monomeric Cp*$_2$YH.

Reaction with 2-Methylpropene: Competitive Recombination and Insertion of Alkene into Monomeric Cp*$_2$YH. The reaction of (Cp*$_2$YH)$_2$ (**2**) with the more crowded 1,1-disubstituted alkene 2-methylpropene occurred substantially slower than with 3-methyl-1-butene. Clean formation of the single-insertion product, Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (**4**), was observed at −75 °C (Scheme 5). Complex **4** is stable below −30 °C, and none of the potential double-insertion product, Cp*$_2$YCH$_2$C(Me)$_2$CH$_2$CH(CH$_3$)$_2$, was seen. Compared with **3**, the ^{1}H NMR resonance of the YCH$_2$ group of **4** appears at lower frequency (δ −0.08 compared with δ 0.27 for **3**) and the ^{13}C NMR spectrum of **4** shows stronger yttrium−carbon coupling ($^1J_{YC} = 51$ Hz compared with 36 Hz for **3**) and weaker carbon−hydrogen coupling ($J_{CH} = 106$ Hz compared with 124 Hz for **3**). The ^{1}H NMR chemical shift of the β-methine hydrogen of **4** appears at a normal chemical shift of δ 1.89 and has a normal $J_{CH} = 121$ Hz, unlike the β-methylene resonance of **3**, which was shifted to dramatically lower frequency at δ −0.12 and has reduced $J_{CH} = 108$ Hz. These spectral differences suggest that **4** has an α-agostic interaction rather than the β-agostic interaction seen for **3**. The difference is attributable to steric problems in forming a β-agostic interaction to the more crowded methine group of **4**.

A kinetic study of the reaction of (Cp*$_2$YH)$_2$ (**2**) and 2-methylpropene at −75 °C showed that the insertion appears first order in hydride dimer, as determined by the linear correlation of ln[**2**$_0$]/[**2**$_t$] vs time. Additionally, at low alkene concentrations the observed rate constant, k_{obs}, is dependent on alkene concentration. A plot of k_{obs} vs [2-methylpropene] shows that, as the alkene concentration is raised, saturation kinetics are reached (Figure 4). Using the combined rate data for dimer dissociation shown in Figure 3, the rate of dimer dissociation at −75 °C was calculated to be 6.7×10^{-4} s^{-1}, which is quite similar to the observed saturation rate 7.1×10^{-4} s^{-1}.

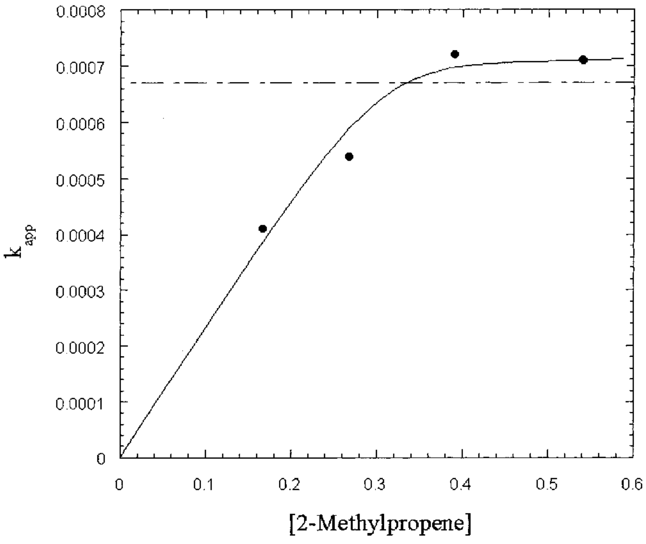
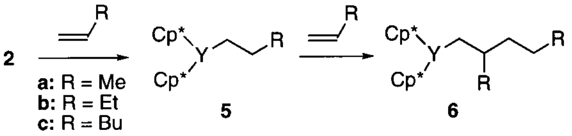


Figure 4. [2-Methylpropene] dependence of k_{obs} in the reaction of **2** with 2-methylpropene at −75 °C.[21] The dashed line indicates the rate of dissociation of dimer **2** determined by 3-methyl-1-butene insertion.

Scheme 6



We interpret this kinetic behavior in terms of competition between reaction of monomer Cp*$_2$YH with itself and with alkene. At low [2-methylpropene], the monomeric intermediate Cp*$_2$YH partitions between recombination to regenerate dimer **2** and reaction with alkene to give **4**. In this concentration range, the kinetics of 2-methylpropene insertion are between half and first order in [**2**] and between zero and first order in alkene. At the high-concentration limit, monomeric intermediate Cp*$_2$YH is efficiently trapped by 2-methylpropene and saturation kinetics are observed.

Reaction with 1-Hexene: Competitive Associative Reaction of Alkene with Dimer. The terminal alkene 1-hexene is less crowded than either 3-methyl-1-butene or 2-methylpropene, and it reacted substantially faster with (Cp*$_2$YH)$_2$ (**2**). Reaction of **2** (0.06 M) with 1-hexene (0.13 M, 1.1 equiv) occurred at −85 °C. A mixture of the single-insertion product Cp*$_2$Y(CH$_2$)$_5$CH$_3$ (**5c**), the double-insertion product Cp*$_2$YCH$_2$CH(Bu)(CH$_2$)$_5$CH$_3$ (**6c**),[12] and unreacted **2** was observed by ^{1}H and ^{13}C NMR spectroscopy (Scheme 6). No triple-insertion products were seen. When the reaction was performed with >2 equiv of 1-hexene, only the double-insertion product **6c** was observed. Similar results were obtained for the reaction of (Cp*$_2$YH)$_2$ (**2**) with propene and 1-butene.

Reaction of **2** with excess 1-hexene under pseudo-first-order conditions was monitored by ^{1}H NMR spectros-

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[12] The single-insertion products **5** appear to have an agostic interaction with the β-hydrogens, on the basis of the upfield shift of these protons. The ^{1}H NMR spectra of double-insertion products **6** are much like those of the similarly substituted complex **4**; consequently, compounds **6** likely have ground-state α-agostic interactions.

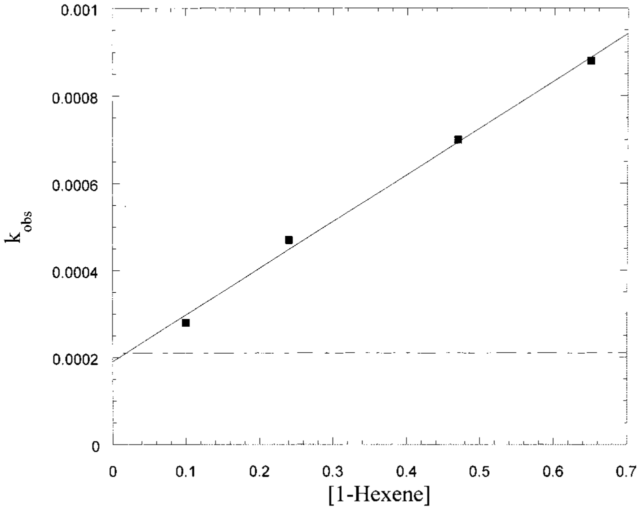


Figure 5. [1-Hexene] dependence of k_{obs} in the reaction of **2** with 1-hexene. The dashed line indicates the rate of dissociation of dimer **2** determined by 3-methyl-1-butene insertion.

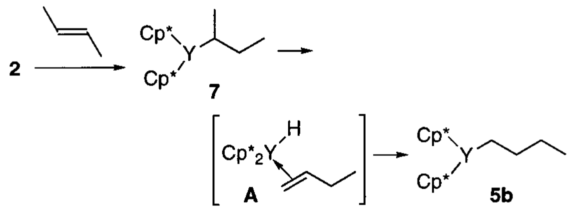
copy at −80 °C. The disappearance of **2** was cleanly first order to >3 half-lives, as shown by the linear correlation of ln[$\mathbf{2}_0$]/[$\mathbf{2}_t$] vs time. Interestingly, variation of the concentration of 1-hexene showed that the rate was also dependent on 1-hexene concentration. A plot of k_{obs} vs [1-hexene] does not pass through the origin, indicating that there is an additional process producing product that is zero order in 1-hexene (Figure 5).

These data suggest that 1-hexene insertion occurs through *both* an associative bimolecular reaction of alkene with dimer **2** and by rapid trapping of Cp*$_2$YH produced by dissociation of **2**. The slope of the 1-hexene dependence, [1.07(5)] × 10^{-4} M^{-1} s^{-1}, corresponds to k_{assoc}, the second-order rate constant for bimolecular insertion, and the intercept, [1.9(2)] × 10^{-4} s^{-1}, is a measure of the first-order rate constant k_{dis} for rate-determining dissociation of dimer **2**. This intercept is predicted to have the same value as the rates of dissociation of dimer **2** obtained from kinetics of 3-methyl-1-butene insertion ([2.2(2)] × 10^{-4} s^{-1} at −80 °C) and from extrapolation of rates obtained from NMR line broadening studies at higher temperature (Figure 3). The close agreement between the intercept of Figure 5 and these independent measures of dimer dissociation rates support these mechanistic proposals.

$$-\mathrm{d}[\mathbf{2}]/\mathrm{d}t = k_{assoc}\,[\mathbf{2}][\text{1-hexene}] + k_{dis}[\mathbf{2}] \qquad (4)$$

Double Insertion of 1-Hexene. Close monitoring of the initial stages of the 1-hexene insertion revealed that the maximum amount of single-insertion intermediate **5c** depended on the concentration of 1-hexene used. For example, at −83 °C the maximum amount of **5c** was 24% of the total yttrium concentration at [1-hexene] = 0.12 M and but was only 12% at [1-hexene] = 0.36 M. This is the expected result for consecutive reactions (**2** → **5c** → **6c**) if the kinetics of formation of **5c** and **6c** have different orders in 1-hexene. The formation of **5c** has been shown to have both a zero-order and a first-order 1-hexene dependence (overall order <1), whereas the production of **6c** from **5c** is first order in 1-hexene.[13]

Scheme 7



The maximum amount of an intermediate that builds up in the course of consecutive reactions depends on the relative rates of production and further reaction of the intermediate. A quantitative relationship for the maximum buildup of an intermediate **5c** is given in eq 5,

$$[\mathbf{5c}]_{max} = [\mathrm{Y}]_0\left(\frac{k_{react}}{k_{form}}\right)^{k_{react}/(k_{form}-k_{react})} \qquad (5)$$

where $[\mathrm{Y}]_0$ is the initial total yttrium concentration, k_{form} is the pseudo-first-order rate constant for the formation of intermediate **5c**, and k_{react} is the pseudo-first-order rate constant for insertion into **5c**.[14] The rate of formation of **5c** is equal to twice the rate of disappearance of dimer **2**. From the observed rate of disappearance of **2** (1.8 × 10^{-4} s^{-1}) in the presence of 0.12 M 1-hexene and from the maximum 24% **5c** observed, the rate of further reaction of intermediate **5c** with 1-hexene was calculated to be 8 × 10^{-4} s^{-1}; this gives a second-order rate constant for reaction of **5c** with 0.12 M 1-hexene of 6.7 × 10^{-3} $M^{-1}s^{-1}$. Similarly, the rate of disappearance of **2** (2.4 × 10^{-4} s^{-1}) in the presence of 0.36 M 1-hexene and the maximum 12% **5c** observed allowed calculation of the rate of 1-hexene insertion into intermediate **5c** of 2.3 × 10^{-3} s^{-1} and a second order rate constant of 6.4 × 10^{-3} $M^{-1}s^{-1}$ ($\Delta G^{\ddagger}$ = 13.7 kcal mol^{-1}). The close similarity of these two calculated second-order rate constants for reaction of **5c** with 1-hexene supports our proposed mechanistic scheme.

Reaction with 2-Butene: Isomerization of Initial Yttrium Alkyl. The internal alkenes *cis-* and *trans-*2-butene required somewhat higher temperature for reaction with (Cp*$_2$YH)$_2$ (**2**). The time-dependent NMR spectra clearly showed that the expected branched insertion product Cp*$_2$YCH(CH$_3$)CH$_2$CH$_3$ (**7**) formed at early reaction times. However, by the time reaction was complete, only the straight-chain insertion product Cp*$_2$Y(CH$_2$)$_3$CH$_3$ (**5b**) was seen (Scheme 7). After 2 h in the reaction with *trans*-2-butene, 30% unreacted dimer **2**, 55% branched isomer **7**, and 15% straight-chain isomer **5b** were seen. Somewhat unexpectedly, reaction of **2** with 2-butene provides a better route to *n*-butylyttrium complex **5b** than reaction with 1-butene, because **5b** reacts with 1-butene to give the double-insertion product **6b** but is unreactive toward 2-butene.

Isomerization of the branched-chain isomer **7** to the straight-chain isomer **5b** is suggested to occur by *β*-hydride elimination and readdition. Similar isomerizations to straight-chain alkylzirconium complexes are seen in hydrozirconation reactions.[15,16] We do not know whether free 1-butene is an intermediate in this isomerization.

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[13] In the reaction of propene with Cp*$_2$YCH$_2$CH$_2$CHMe$_2$, we have shown that the reaction is first order in alkene and in yttrium alkyl.[7e]

[14] Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; pp 71−75.

Under similar conditions, the insertion of *cis*-2-butene ($t_{1/2} \approx 45$ min) proceeded faster than that of *trans*-2-butene ($t_{1/2} \approx 70$ min). The rate of disappearance of dimer **2** in reaction with *trans*-2-butene at −66 °C occurred at a rate of $\sim 3 \times 10^{-4}$ s^{-1}. This is about 6 times slower than the 1.8×10^{-3} s^{-1} rate of dissociation of dimer **2** at −66 °C estimated from Figure 3. If insertion is much slower than dimer dissociation, then kinetics would be predicted to be half order in $(Cp^*_2YH)_2$ (**2**) and first order in 2-butene. Kinetic traces show that the disappearance of **2** is not cleanly half or first order. Apparently, the reaction of monomeric intermediate Cp^*_2YH with alkene is competitive with the re-formation of **2**.

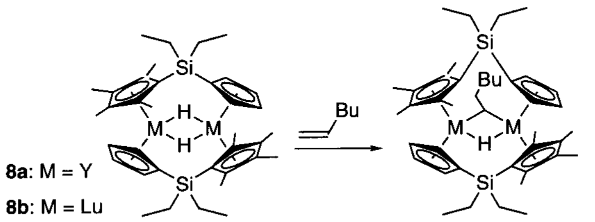
Discussion

The reactions of 3-methyl-1-butene and of 2-methylpropene with $(Cp^*_2YH)_2$ (**2**) provide very clean syntheses of $Cp^*_2YCH_2CH_2CH(CH_3)_2$ (**3**) and $Cp^*_2YCH_2CH(CH_3)_2$ (**4**), respectively. The key to these selective syntheses is the low reactivity of the resultant yttrium alkyls toward a second insertion of alkene. In contrast, terminal alkenes such as 1-butene gave mixtures of single- and double-alkene-insertion products. An indirect route to *n*-butylyttrium complex **5b** was found that involved initial addition of **2** to 2-butene to give the 2-butylyttrium complex **7**, which rearranged to **5b** by metal hydride addition elimination. **3** and **4** will be useful for studying the rates of insertion of alkenes into metal alkyl complexes.

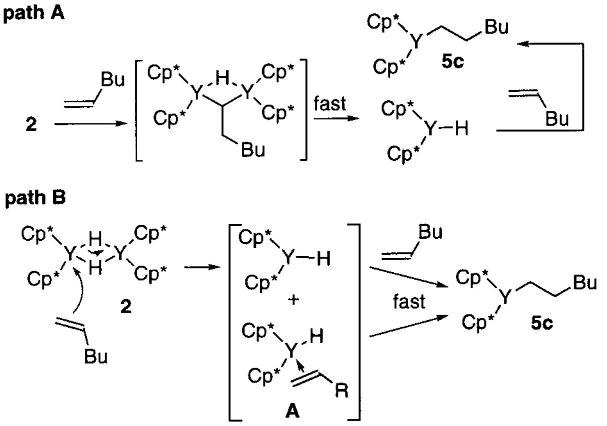
Earlier we observed that Cp^*_2Y−alkyl complexes react with 1-alkenes at or near −100 °C;[7e] no reaction between $(Cp^*_2YH)_2$ (**2**) and alkenes is observed at these temperatures. In contrast, the insertion of alkenes into metal hydrides is normally much more rapid than into metal−alkyls.[16] Our qualitative result indicates that the bridging hydrides of **2** are much less reactive than the terminal hydride of Cp^*_2YH; that is, dimerization greatly decreases the reactivity of metal hydrides.

A full range of dissociative and associative mechanisms for reaction of alkenes with **2** was found. For the most crowded and least reactive alkenes studied, 2-butene and 2-methylpropene, reaction with **2** occurred more slowly than the rate of dissociation of dimer **2** determined by NMR line-broadening techniques. Kinetic studies established reversible dissociation of **2** to monomeric Cp^*_2YH followed by competitive trapping by alkene and recombination to regenerate **2**. Kinetic studies of a somewhat less crowded alkene, 3-methyl-1-butene, showed that reaction occurred by rate-limiting dissociation of dimer **2** followed by efficient trapping of the intermediate Cp^*_2YH by alkene. The reaction showed no dependence on [3-methyl-1-butene] and proceeded at the same rate as dimer dissociation. The least crowded terminal alkenes such as 1-hexene reacted with **2** at a rate faster than dimer dissociation. Kinetic studies established a two-component rate law involving a second-order term for direct attack of alkene on the dimer and a first-order term involving rate-determining dimer dissociation followed by rapid alkene reaction with monomeric Cp^*_2YH.

Scheme 8



Scheme 9



While insertion of alkenes into bridging yttrium hydrides is known,[17,18] the direct associative reaction of 1-hexene with the dimer $(Cp^*_2YH)_2$ (**2**) is somewhat surprising, since it has been shown that the rate of 1-hexene insertion into the strictly dimeric lutetium hydride **8b** is 10^8 times slower than insertion into monomeric Cp^*_2LuH (Scheme 8).

The associative insertion can be envisioned to go via one of two pathways (Scheme 9).[19] First, the alkene might insert into one of the dimer Y−H, bonds producing a bridging yttrium alkyl hydride. Alkyl groups are poor bridging ligands, and the dissociation of the alkyl-bridged intermediate would be expected to be faster than that of the dihydride. Dissociation followed by rapid trapping of the monomeric yttrium hydride would give rise to the observed kinetics (path A). Second, 1-hexene might undergo an associative substitution, producing Cp^*_2YH and the alkene complex **A**, followed once again by rapid trapping of the Cp^*_2YH (path B). Although these two pathways are kinetically indistinguishable, we favor path B on the basis of the low reactivity of bridging hydrides previously mentioned (Scheme 8).[18,19] Presumably, complex **8a** is forced to insert alkenes through a path similar to path A, which was relatively slow at room temperature. This would seem to implicate the associative displacement mecha-

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(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.

(16) We have drawn the intermediate as a 1-butene coordinated hydride because no free 1-butene is observed, although it remains possible that free 1-butene and $(Cp^*_2YH)_2$ are formed.

(17) (a) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228. (b) Schaverien, C. J. *Organometallics* **1994**, *13*, 69. (c) Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 11. (d) Voskoboynikov, A. Z.; Shestakova, A. K.; Beletskaya, I. P. *Organometallics* **2001**, *20*, 2794.

(18) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

(19) In related studies, we have found that the rates of alkene insertions into Cp^*_2YH−THF have an [alkene] dependence, indicating associative insertion of alkenes: Klein, J. F. Ph.D. Thesis, University of Wisconsin−Madison, Madison, WI, 1999.

nism (path B) for the rapid insertion of 1-hexene into $(\mathrm{Cp^*_2YH})_2$ (**2**) at −70 °C.

The reactions of terminal alkenes with **2** initially gave mixtures of single- and double-alkene-insertion products but no triple-insertion products. More highly substituted alkenes gave only single-insertion products. The $\Delta G^\ddagger$ barrier for 1-hexene insertion into $\mathrm{Cp^*_2Y(CH_2)_5CH_3}$ was determined to be 13.7 kcal mol^{-1} at −83 °C. In contrast, 3-methyl-1-butene and 2-methylpropene insert a single time, and the resulting yttrium−alkyl complexes do not insert a second equivalent of alkene even at −30 °C ($\Delta G^\ddagger$ > 19 kcal mol^{-1}). The steric environment of the alkene is not solely responsible for the observed reactivity differences. The steric environment of the yttrium−alkyl also greatly influences the reactivity. This is shown by the fact that at −80 °C propene inserts and twice then stops; thus, propene insertion into $\mathrm{Cp^*YCH_2CH_2CH_3}$ (**5a**) is much faster than into $\mathrm{Cp^*_2YCH_2CH(CH_3)CH_2CH_2CH_3}$ (**6a**). This behavior is the result of the exquisite sensitivity of the reaction of alkylyttrium complexes with alkenes to the presence of a β-alkyl substituent on the yttrium alkyl or of a second allylic alkyl substituent on the alkene. Quantitative investigations of steric effects on the insertion of alkenes into yttrium−alkyl bonds are underway.

Experimental Section

General Considerations. All compounds were manipulated in an inert-atmosphere glovebox or using standard high-vacuum techniques. All reactions were performed in flame-dried 1.9 mL medium-walled J. Young resealable NMR tubes equipped with a Teflon stopcock. ^{1}H NMR spectra were obtained on a Varian Unity 500 operating at 500 MHz (^{1}H NMR) and 126 MHz (^{13}C NMR). DEPT-90, DEPT-135, 1D nOe, 1D TOCSY, ^{1}H COSY, and ^{1}H−^{13}C HSQC spectra were obtained with a 5 mm gradient-bbswg probe. Spectrometer temperatures were measured using a methanol thermometer or a thermocouple. Line broadening due to dynamic exchange was determined by simulating NMR spectra using the WinDNMR program.[2020−21]

Methylcyclohexane-d_{14} (Cambridge Isotopes) and pentane-d_{12} (Cambridge Isotopes) were distilled from sodium/potassium alloy. Propene (Aldrich), 1-butene (Aldrich), 3-methyl-1-butene (Aldrich), isobutylene (Aldrich), $\mathrm{H_2}$ (Liquid Carbonic), and $\mathrm{D_2}$ (Cambridge Isotopes) were used as received. 1-Hexene (Aldrich) was distilled from $\mathrm{NaBH_4}$. $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ was prepared by a known procedure.[9a,9b]

Hydride Exchange Kinetics: $(\mathrm{Cp^*_2YD})_2$ + $(\mathrm{Cp^*_2YD})_2$. A solution of $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ (9 mg, 0.017 mmol) in 200 mL of methylcyclohexane-d_{14} was degassed by three freeze−pump−thaw cycles, and 1 atm of $\mathrm{D_2}$ was added at −196 °C. This solution was shaken periodically over 10 min at 0 °C to form $(\mathrm{Cp^*_2YD})_2$ (**2-DD**). Similarly, a solution of $(\mathrm{Cp^*_2YH})_2$ (**2**) was prepared by addition of $\mathrm{H_2}$ to a solution of $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ (0.024 mmol) in 200 mL of methylcyclohexane-d_{14}. A two-layered mixture was prepared by condensing a layer of pentane-d_{12} (~75 mL) onto the solution of **2-DD**. The solution of **2** was taken up in a syringe and added to the frozen **2-DD** mixture. This produced a three-layered solution containing **2** (top layer), neat pentane-d_{12} (middle layer), and **2-DD** (bottom layer). The NMR tube was shaken at −98 °C and placed directly into the NMR probe. ^{1}H NMR spectra were acquired over a range of temperatures (−80 to −20 °C).

NMR Line Broadening of $(\mathrm{Cp^*_2YH})_2$ (2). A solution of **2** in methylcyclohexane-d_{14} (200 mL) and pentane-d_{12} (200 mL) was prepared from $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ (0.05 mmol) and 1 atm of $\mathrm{H_2}$ at 0 °C. The solution was degassed by three freeze−pump−thaw cycles, and ^{1}H NMR spectra were acquired over a range of temperatures (−60 to 50 °C).

Line Broadening of $(\mathrm{Cp^*_2YH})_2$ (2) in the Presence of $\mathrm{H_2}$. A solution of **2** was produced by hydrogenation of $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ (9.1 mg, 0.018 mmol) under 1 atm of $\mathrm{H_2}$ as described above. The solution was not degassed. ^{1}H NMR spectra were acquired at a range of temperatures (−95 to 50 °C).

Typical Procedure for Kinetics of the Insertion Reaction of $(\mathrm{Cp^*_2YH})_2$ (2) with Alkenes. An aliquot of a standard solution (0.04 M) of $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ (200 mL, 8 mmol) in methylcyclohexane-d_{14} was placed in a resealable medium-walled NMR tube. Pentane-d_{12} (200 μL) was condensed into this solution. The resulting solution was degassed by three freeze−pump−thaw cycles, and 1 atm of $\mathrm{H_2}$ was added at −196 °C. This solution was warmed to 0 °C (3−4 atm of $\mathrm{H_2}$) and shaken periodically over 10 min to form **2**. After the solution was degassed by three freeze−pump−thaw cycles, 3-methyl-1-butene (0.14 mmol, measured using a monometer) was added at −196 °C. The frozen solution was place in the precooled (−130 °C) NMR probe to melt. The tube was ejected, shaken briefly, and reinserted. ^{1}H NMR spectra were obtained at −80 °C. Concentrations were determined by integration of Cp* resonances vs $\mathrm{CH_2(SiMe_3)_2}$ internal standard.

Insertion of 3-Methyl-1-butene: $\mathrm{Cp^*_2YCH_2CH_2CH(CH_3)_2}$ (3). ^{1}H NMR (500 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ −0.12 (td, $^3J_{\mathrm{HH}} = 6.6$, 6.1 Hz, ↔ 0.27, ↔ 1.63, $\mathrm{C}\mathit{H}_2\mathrm{CH}$), 0.27 (m, ↔ −0.12, $\mathrm{YCH_2}$), 0.93 (d, ↔ 1.63, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.63 (m, ↔ 0.93, ↔ −0.12, $\mathrm{CH_2C}\mathit{H}$), 1.90 (s, $\mathrm{C_5Me_5}$). ^{13}C NMR (125.7 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ 10.8 (q, $J_{\mathrm{CH}} = 126$ Hz, ↔ 1.90, $\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 23.6 (q, $J_{\mathrm{CH}} = 118$ Hz, ↔ 0.93, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 34.5 (d, $J_{\mathrm{CH}} = 122$ Hz, ↔ 1.63, $\mathrm{CH_2}\mathit{C}\mathrm{H}$), 38.9 (td, $J_{\mathrm{CH}} = 124$ Hz, $^1J_{\mathrm{YC}} = 36$ Hz, ↔ 0.027, $\mathrm{Y}\mathit{C}\mathrm{H_2}$), 46.7 (t, $J_{\mathrm{CH}} = 108$ Hz, ↔ −0.12, $\mathit{C}\mathrm{H_2CH}$), 116.7 (s, $\mathit{C}_5\mathrm{Me_5}$). Spectral assignments were aided by DEPT-135, 1D TOCSY, ^{1}H COSY and ^{1}H-^{13}C HSQC experiments. COSY and HSQC correlations are indicated by ↔.

Insertion of 2-Methylpropene: $\mathrm{Cp^*_2YCH_2CH(CH_3)_2}$ (4). ^{1}H NMR (500 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ −0.08 (dd, $^3J_{\mathrm{HH}} = 7.5$, $^2J_{\mathrm{YH}} = 3.4$ Hz, ↔ 1.89, $\mathrm{YCH_2}$), 0.67 (d, $^3J_{\mathrm{HH}} = 6.5$, ↔ 1.89, $\mathrm{CH(C}\mathit{H}_3)_2$), 1.89 (m, ↔ −0.08, ↔ 0.67, $\mathrm{CH_2C}\mathit{H}$), 1.92 (s, $\mathrm{C_5Me_5}$). ^{13}C NMR (125.7 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ 11.0 (q, $J_{\mathrm{CH}} = 126$ Hz, ↔ 1.92, $\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$), 27.1 (d, $J_{\mathrm{CH}} = 121$ Hz, ↔ 1.89, $\mathrm{CH_2}\mathit{C}\mathrm{H}$), 27.9 (q, $J_{\mathrm{CH}} = 119$ Hz, ↔ 0.67, $\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 44.4 (td, $J_{\mathrm{CH}} = 106$ Hz, $J_{\mathrm{YC}} = 51$ Hz, ↔ −0.08, $\mathrm{YCH_2}$), 117.6 (s, $\mathit{C}_5\mathrm{Me_5}$).

Insertion of 1-Hexene: (a) $\mathrm{Cp^*_2YCH_2(CH_2)_4CH_3}$ (5c). ^{1}H NMR (500 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ 0.08 (br, ↔ 0.30, ↔ 1.57, $\mathrm{YCH_2C}\mathit{H}_2$), 0.30 (br, ↔ 0.08, $\mathrm{YCH_2}$), 0.93 (t, $J = 6.6$ Hz, ↔ 1.32, $\mathrm{CH_2C}\mathit{H}_3$), 1.28 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.32 (m, ↔ 0.93, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.57 (m, ↔ 0.08, $\mathrm{YCH_2CH_2C}\mathit{H}_2$), 1.91 (s, $\mathrm{C_5Me_5}$). ^{13}C{^{1}H} NMR (125.7 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ 13.26 ($\mathrm{C_5}\mathit{Me}_5$), 20.7 ($\mathrm{CH_3}$), 32.0 ($\mathrm{CH_2}$), 35.0 ($\mathrm{CH_2}$), 35.5 ($\mathrm{CH_2}$), 38.7 (d, $J_{\mathrm{YC}} = 38$ Hz, $\mathrm{YCH_2}$), 115.4 ($\mathit{C}_5\mathrm{Me_5}$).

(b) $\mathrm{Cp^*_2YCH_2CH(Bu)CH_2(CH_2)_4CH_3}$ (6c). ^{1}H NMR (500 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ −0.35 (m, ↔ 1.62, $\mathrm{YC}\mathit{H}_2$), 0.72−0.78 (br, 3H), 0.88 (m, 6H), 1.00 (m, 2H), 1.09 (m, 2H), 1.20−1.30 (m, 9H), 1.62 (m, ↔ −0.35, $\mathrm{YCH_2C}\mathit{H}$), 1.89 (s, $\mathrm{C_5Me_5}$). ^{13}C NMR (125.7 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ 116.1 (s, $\mathit{C}_5\mathrm{Me_5}$), 42.8 (d, $J_{\mathrm{YC}} = 52$ Hz, $\mathrm{YCH_2}$), 31.2 ($\mathrm{CH_2}$), 30.3 ($\mathrm{CH_2}$), 30.1 ($\mathrm{CH_2}$), 29.5 ($\mathrm{CH_2}$), 28.8 ($\mathrm{CH_2}$), 22.8 ($\mathrm{CH_2}$), 22.3 ($\mathrm{CH_2}$), 21.5 ($\mathrm{CH_2}$), 13.3 ($\mathrm{CH_3}$), 13.2 ($\mathrm{CH_3}$), 13.1 (CH), 9.9 ($\mathrm{C_5}\mathit{Me}_5$). Spectral assignments were aided by ^{1}H COSY, 1D TOCSY, and DEPT-135.

Insertion of Propene: (a) $\mathrm{Cp^*_2YCH_2CH_2CH_3}$ (5a). ^{1}H NMR (500 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ 0.15 (m, ↔ 0.32, ↔ 1.22, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 0.32 (m, ↔ 0.15, $\mathrm{YC}\mathit{H}_2$), 1.22 (t, ↔ −0.32, $\mathrm{CH_2C}\mathit{H}_3$), 1.908 (s, $\mathrm{C_5Me_5}$). ^{13}C{^{1}H} NMR (125.7 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ 10.86 ($\mathrm{C_5}\mathit{Me}_5$), 20.94 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 29.84 ($\mathit{C}\mathrm{H_2CH_3}$), 42.75 (d, $\mathrm{YCH_2}$, $J_{\mathrm{YC}} = 34$ Hz), 116.81 ($\mathit{C}_5\mathrm{Me_5}$).

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[20] Reich, H. J. *J. Chem. Educ.* **1995**, *72*, 1086.

[21] Reaction rates at low [2-methylpropene] were determined by kinetic fits assuming first-order disappearance of $(\mathrm{Cp^*_2YH})_2$, but the true order is <1.

(b) $\mathrm{Cp^*_2YCH_2CH(CH_3)(CH_2)_2CH_3}$ (6a). ^{1}H NMR (500 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ −0.59 (m, ↔ 0.01, ↔ 1.76, $\mathrm{YCH}\mathit{H}$), 0.01 (m, ↔ −0.59, ↔ 1.76, $\mathrm{YC}\mathit{H}\mathrm{H}$), 0.69 (br d, ↔ 1.76, $\mathrm{CH(C}\mathit{H_3}\mathrm{)CH_2}$), 0.71 (m, $\mathrm{C}\mathit{H}\mathrm{HCH_3}$), 0.77 (m, $\mathrm{CHC}\mathit{H}\mathrm{H}$), 0.89 (br t, $\mathrm{CH_2C}\mathit{H_3}$), 1.05 (m, $\mathrm{CH}\mathit{H}\mathrm{CH_3}$), 1.24 (m, $\mathrm{CHCH}\mathit{H}$), 1.76 (m, $\mathrm{C}\mathit{H}\mathrm{CH_2}$), 1.89 (s, $\mathrm{C_5Me_5}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ 9.74 (↔ 1.89, $\mathrm{C_5}\mathit{Me}_5$), 13.65 (↔ 0.89, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 20.34 (↔ 0.71, ↔ 1.05, $\mathit{C}\mathrm{H_2CH_3}$), 26.81 (↔ 0.69, $\mathrm{CH}\mathit{C}\mathrm{H_3}$), 33.32 (↔ 1.76,$\mathit{C}\mathrm{HCH_2}$), 43.83 (↔ 0.77, ↔ 1.24, $\mathrm{CH}\mathit{C}\mathrm{H_2}$), 43.95 (d, J_{YC} = 49 Hz, ↔ −0.59, ↔ 0.01, $\mathrm{YCH_2}$), 116.08 ($\mathit{C}_5\mathrm{Me_5}$). Spectral assignments were aided by DEPT-135, 1D TOCSY, ^{1}H COSY, and $^1\mathrm{H}-^{13}\mathrm{C}$ HSQC. COSY and HSQC correlations are indicated by ↔.

Insertion of 1-Butene: (a) $\mathrm{Cp^*_2YCH_2CH_2CH_2CH_3}$ (5b). ^{1}H NMR (500 MHz, −65 °C, $\mathrm{C_6D_{11}CD_3}$): δ 0.03 (br, ↔ 0.25, ↔ 1.55, $\mathrm{YCH_2C}\mathit{H_2}$), 0.25 (br, ↔ 0.03, $\mathrm{YCH_2}$), 0.90 (t, ↔ 1.55, $\mathrm{CH_2C}\mathit{H_3}$), 1.55 (br, ↔ 0.90, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 1.91 (s, $\mathrm{C_5Me_5}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, −50 °C, $\mathrm{C_6D_{11}CD_3}$): δ 9.52 (↔ 1.91, $\mathrm{C_5}\mathit{Me}_5$), 12.87 (↔ 0.90, $\mathrm{CH_3}$), 28.16 (↔ 1.55, $\mathit{C}\mathrm{H_2CH_3}$), 37.54 (↔ 0.03, $\mathrm{YCH_2}\mathit{C}\mathrm{H_2}$), 38.54 (d, J_{YC} = 39 Hz, ↔ 0.25, $\mathrm{YCH_2}$), 115.49 ($\mathit{C}_5\mathrm{Me_5}$).

(b) $\mathrm{Cp^*_2YCH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3}$ (6b). ^{1}H NMR (360 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ −0.40 (m, ↔ 1.60, $\mathrm{YCH_2}$), 0.63 (t, J = 6.4 Hz, ↔ 0.80, $\mathrm{CHCH_2C}\mathit{H_3}$), 0.79 ($\mathrm{CH_2C}\mathit{H}\mathrm{HCH_3}$), 0.80 ($\mathrm{CH(C}\mathit{H}\mathrm{HCH_3}$), 0.88 (t, $\mathrm{CH_2CH_2C}\mathit{H_3}$), 0.96−1.05 ($\mathrm{CHC}\mathit{H_2}$), 1.27 ($\mathrm{CH_2CH}\mathit{H}\mathrm{CH_3}$), 1.30 ($\mathrm{CH_2C}\mathit{H_2}\mathrm{CH_3}$), 1.42 ($\mathrm{CH(CH}\mathit{H}\mathrm{CH_3}$), 1.60 (↔ −0.40, ↔ 0.80, CH), 1.90 (s, $\mathrm{C_5Me_5}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (90 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ 9.86 (↔ 1.90, $\mathrm{C_5}\mathit{Me}_5$), 10.55 (↔ 0.63, $\mathrm{CHCH_2}\mathit{C}\mathrm{H_3}$), 13.27 (↔ 0.88, $\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_3}$), 23.33 (↔ 1.30, $\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_3}$), 29.13 (↔ 0.96−1.05, $\mathrm{CH}\mathit{C}\mathrm{H_2CH_2}$), 33.09 (↔ 0.80, ↔ 1.42, $\mathrm{CH}\mathit{C}\mathrm{H_2CH_3}$), 41.06 (↔ 0.79, ↔ 1.27,$\mathit{C}\mathrm{H_2CH_2CH_3}$), 42.54 (d, J_{YC} = 56 Hz, $\mathrm{YCH_2}$), 116.09 ($\mathit{C}_5\mathrm{Me_5}$). The ^{1}H NMR spectrum is broad and nondescript, and so assignments are based on 1D TOCSY, ^{1}H COSY, and $^1\mathrm{H}-^{13}\mathrm{C}$ HSQC.

Insertion of *cis*- or *trans*-2-Butene: $\mathrm{Cp^*_2YCH(CH_3)CH_2CH_3}$ (7). ^{1}H NMR (500 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ 0.32 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, ↔ 0.68, $\mathrm{YCHC}\mathit{H_3}$), 0.68 (br, ↔ 0.32, ↔ 1.68, YCH), 0.76 (m, ↔ 1.68, ↔ 1.78, $\mathrm{CH_2C}\mathit{H_3}$), 1.68 (m, ↔ 0.76, ↔ 0.68, $\mathrm{C}\mathit{H}\mathrm{HCH_3}$), 1.78 (m, ↔ 0.76, $\mathrm{CH}\mathit{H}\mathrm{CH_3}$), 1.86 ($\mathrm{C_5(CH_3)_5}$), 1.89 ($\mathrm{C_5(CH_3)_5}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (90 MHz, −60 °C, $\mathrm{C_6D_{11}CD_3}$): δ 17.13 (↔ 0.76, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 23.64 (↔ 0.32 $\mathrm{YCH}\mathit{C}\mathrm{H_3}$), 28.62 (↔ 1.68 ↔ 1.78, $\mathrm{CH_2}$), 44.88 (d, J_{YC} = 36 Hz, ↔ 0.68, $\mathrm{YCH_2}$). Spectral assignments were aided by DEPT-135, 1D TOCSY, ^{1}H COSY, and $^1\mathrm{H}-^{13}\mathrm{C}$ HSQC experiments. COSY and HSQC correlations are indicated by ↔. This product was only observed at low conversion along with various amounts of **5b**.

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Supporting Information Available: Figures giving kinetic data for 3-methyl-1-butene insertion, the NMR spectrum of hydride and $\mathrm{H_2}$ broadening, the reaction profile for 1-hexene insertion, and representative kinetic traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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