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Structural Dependence of Thermodynamics of Alkene Binding to Yttrium Alkyl Complexes and of Kinetics of Alkyl Migration to Coordinated Alkenes

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Abstract: Agostic interactions in yttrium alkyls are structure dependent. Primary alkyl yttrium complexes have β-CH$_2$ agostic interactions at low temperature, but a shift toward α-agostic interactions occurs on warming. For the more crowded β-disubstituted yttrium alkyls, an α-CH$_2$ agostic interaction is seen. The thermodynamics of alkene binding to the primary alkyl yttrium complex Cp*$_2$YCH$_2$CH$_2$CH(CH$_3$)$_2$ (**2**) depend strongly on the structure of the alkene. A single allylic substituent on the alkene has a small effect on alkene binding, but a second allylic substituent has a large destabilizing effect. Propene binding to yttrium alkyls is largely independent of the nature of the alkyl ligand. Equilibrium constants for propene binding to *n*-, γ-substituted, β-substituted, and secondary alkyl yttrium complexes are similar. The rate of migration of an alkyl group to a coordinated alkene depends strongly on the structure of the alkyl group: *n*-alkyl ≈ γ-substituted ≫ β-substituted ≫ α-substituted. The ∼200-fold slower insertion of propene into Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (**6**) than that into Cp*$_2$YCH$_2$CH$_2$CH(CH$_3$)$_2$ (**2**) is therefore due to kinetically slow migration of the β-disubstituted alkyl group of **6** and not to differences in the equilibrium binding of propene. Processes related to chain transfer and site epimerization at the metal center are also reported.

Groups 3 and 4 metallocene complexes are thought of as soluble, single-site analogues of heterogeneous Ziegler−Natta alkene polymerization catalysts.[1] In contrast to heterogeneous catalysts, metallocenes produce polymers that have narrow, tunable molecular weight distributions and microstructures that can be controlled by simple changes in metal ligation. Furthermore, metallocenes are superior to conventional catalysts in their ability to incorporate longer 1-alkenes into polymers during copolymerization of higher 1-alkenes with ethylene or propene.[2] Because polymer properties are altered by the degree of comonomer incorporation, control over copolymerization is highly desirable.[3]

The generally accepted mechanism of metallocene-catalyzed alkene polymerization involves chain growth via alkene insertion into a metal alkyl bond. This is proposed to occur by a two-step process involving initial alkene coordination to a transition metal alkyl fragment to form a metal-alkyl-alkene complex,[4,5] followed by alkyl migration to the coordinated alkene monomer. In this paper, we will use the term "alkene insertion" to describe

the net result of the two-step process. Quantitative assessments of the effects of the metal-alkyl and alkene substituents on the equilibrium constants for formation of metal-alkyl-alkene complexes and on the rates of alkyl migration to the coordinated alkene are necessary to fully understand and ultimately control degrees of comonomer incorporation in metallocene-catalyzed alkene copolymerizations.[6]

Here we report our studies of d⁰-yttrium alkyl complexes as models for intermediates in metallocene-catalyzed alkene po-

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lymerization. We have found that substituents on the metal alkyl fragment control whether α- or β-agostic interactions are seen in the yttrium alkyls. Substituents on the yttrium alkyl have little affect on the ability of the yttrium alkyl to coordinate propene, but substituents on the alkene are crucial in controlling the equilibrium constant for alkene coordination. Substituents on both the alkyl and the alkene units of yttrium-alkyl-alkene complexes exert major influence on the rates of alkyl migration to the coordinated alkene. We have also studied processes related to chain transfer and stereochemical inversion at the metal center that are known to affect the properties of the polymer by lowering molecular weights or changing polymer microstructure.

Agostic Interactions in Yttrium Alkyl Complexes. In a paper describing our detailed mechanistic studies of the formation of yttrium alkyls from alkenes and $(Cp*_2YH)_2$,[7] we suggested that yttrocene alkyl complexes adopt ground-state structures stabilized by agostic interactions. Agostic interactions have been shown to be important for the stabilization of ground- and transition-state structures of d^0-metal alkyls during their catalysis of alkene polymerization.[8,9] Agostic interactions are characterized by low energy C−H vibrations and decreased C−H coupling constants.[10] Significant changes in chemical shift upon partial deuteration also provide evidence for agostic interactions because C−H bonds form stronger agostic interactions than C−D bonds. Recently, we suggested that the Y−C (^{89}Y, 100%, $I = {}^1/_2$) coupling constants in $Cp*_2YR$ complexes are diagnostic for the type of agostic interaction: Y−C coupling constants of <40 Hz are indicative of β-agostic interactions, while Y−C coupling constants of >45 Hz are seen for α-, γ-, or perhaps no agostic interaction. Here we present direct evidence for the types of agostic interactions in a range of yttrium alkyls.
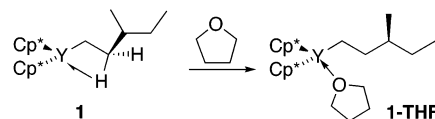
$Cp*_2YCH_2CH_2R$ Have β-Agostic Interactions at Low Temperature. $Cp*_2YCH_2CH_2CH(CH_3)CH_2CH_3$ (**1**) was prepared by reaction of $(Cp*_2YH)_2$ with 3-methyl-1-pentene at −50 °C in methylcyclohexane-d_{14} (Scheme 1). On the basis of the observations of a small $J_{YC} = 36$ Hz and of a lower frequency chemical shift for the β-protons (δ −0.07, −0.20) relative to the α-protons (δ 0.25), **1** is proposed to be stabilized by a β-agostic interaction. The larger than expected $J_{\alpha-CH} = 124$ Hz and the smaller than expected $J_{\beta-CH} = 110$ Hz support the presence of a β-agostic interaction (Table 1).[11]

To better determine the coupling constants expected for a nonagostic complex, **1** was treated with THF to quantitatively form the THF complex (**1-THF**). Because coordination of THF is known to disrupt agostic interactions,[12] the NMR of **1-THF**

Table 1. Selected NMR Characteristics of $Cp*_2YR$ Complexes at −90 °C

compound	J_{YC} (Hz)	$J_{\alpha-CH}$ (Hz)	$J_{\beta-CH}$ (Hz)	δ_α (ppm)	δ_β (ppm)
1	36	124	110	0.25	−0.07−0.20
1-d_β				0.25	−0.27, −0.42
1-THF	53	107	124	−0.65, −0.51	1.29, ∼1.86
2	36	124	108	0.22	−0.16
2-d_β				0.22	−0.36
3	38			0.25	0.03
4	39	119	119	1.00	0.37 syn, 1.80 anti
4-d_β				0.97	0.07 syn, 1.77 anti
5	36			0.66	0.30 (CH₃), 1.70, 1.78 (CH₂)
6	51	106	121	−0.08	1.89
6-d_α				−0.22	1.88
6-THF				−0.54	1.71
6-THF-d_α				−0.58	∼1.7

Scheme 1

reveals the characteristics of a nonagostic complex. Coordination of THF in **1-THF** causes an inversion of the relative chemical shifts of the α- and β-proton as compared with those of **1**. In **1-THF**, the β-protons (δ 1.29, ∼1.86) move to higher frequency than the α-protons (δ −0.51, −0.65), indicating that the agostic interaction has been lost. The $J_{\beta-CH} = 124$ Hz of **1-THF** is consistent with a normal sp³ C−H bond, and the $J_{\alpha-CH} = 107$ Hz is consistent with an sp³ carbon bound to an electropositive element.[13]

Comparison of the NMR characteristics of **1** (β-agostic) and **1-THF** (nonagostic) shows that the β-agostic interaction increases $J_{\alpha-CH}$, decreases $J_{\beta-CH}$, and decreases J_{YC}. These changes can be explained given that the Y−C_α−C_β angle must decrease to accommodate an agostic interaction. The smaller Y−C_α−C_β angle will decrease the s-character in the Y−C_α bond, thus increasing the s-character in the α-CH bonds. The increase in $J_{\alpha-CH}$ reflects this increase in s-character in the α-CH bonds, and the smaller J_{YC} is expected for a decrease in the s-character of the Y−C bond.[14] The decrease in J_{β}-CH, although modest, is diagnostic of an agostic interaction.

Confirmation of the presence (or absence) of an agostic interaction was sought by partial deuteration of the β-position of the alkyl group of **1**. Isotopic perturbation of the chemical shift (IP) is expected upon partial deuteration of any position involved in an agostic interaction because of the preference for deuterium to concentrate in the stronger nonagostic bond than in the weaker agostic bond.[10] Specifically, if there is a β-agostic interaction, monodeuteration of the β-position will shift the β-hydrogen ¹H NMR resonance to lower frequency than the resonance in its all protio analogue.

Reaction of $(Cp*_2YD)_2$[15] with 3-methyl-1-pentene at −50 °C produced a 1:1 mixture of syn- and anti-isomers of $Cp*_2YCH_2$-$CHDCH(CH_3)CH_2CH_3$ (**1-d_β**) (Scheme 2). At −100 °C, the β-CHD ¹H NMR chemical shift for *syn*-**1-d_β** is δ −0.27, and for *anti*-**1-d_β** it is δ −0.42. For comparison, the chemical shift

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(11) Typically, $J_{\alpha-CH} \approx 110$ Hz and $J_{\beta-CH} \approx 125$ Hz for a nonagostic alkyl.

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(15) $(Cp*_2YD)_2$ was synthesized by treatment of $Cp*_2YCH[Si(CH_3)_3]_2$ with D₂.
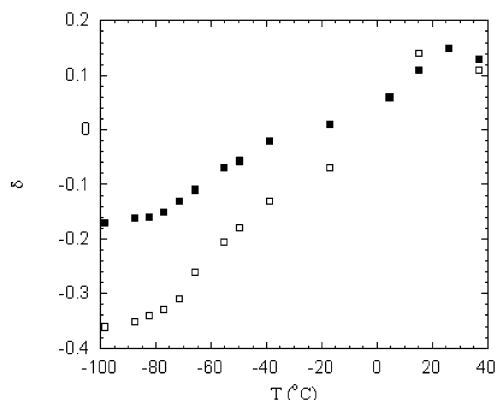
Figure 1. Chemical shifts (δ) of the β-H of **2** (■) and **2-d_β** (□) as a function of temperature.

Scheme 2
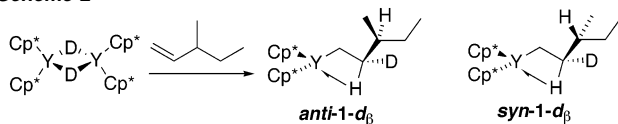
for the *syn*-β-CH of **1** is -0.07, and it is -0.20 for the *anti*-β-CH. The significant IPs of -0.20 ppm for the syn position and -0.22 ppm for the anti position provide convincing evidence for the proposed β-agostic interaction.

For the similar compound $Cp*_2YCH_2CH_2CH(CH_3)_2$ (**2**), evidence for a β-agostic ground state is provided by the observation of a small $J_{YC} = 36$ Hz and of a low-frequency (δ -0.16) resonance for the β-hydrogens. Further evidence for a β-agostic interaction was obtained from the NMR spectrum of the monodeuterated analogue $Cp*_2YCH_2CHDCH(CH_3)_2$ (**2-d_β**).[16] The ^{1}H NMR resonance of the β-hydrogen of **2-d_β** (δ -0.36 at -90 °C) is shifted to lower frequency ($\Delta\delta_{IP} = -0.20$ ppm) as compared with that of **2** ($\delta = -0.16$), consistent with the presence of a β-agostic interaction.

Like **1** and **2**, the straight-chain alkyl complex $Cp*_2$-$YCH_2(CH_2)_4CH_3$ (**3**) has a $J_{YC} < 40$ and β-hydrogens (δ 0.03) that resonate at lower frequency than the α-hydrogens (δ 0.25). Therefore, it is likely that **3** has a β-agostic interaction at low temperature.

β-Agostic Interactions in $Cp*_2YCH_2CH_2R$ Decrease at Higher Temperature. Interestingly, the ^{1}H NMR chemical shifts of the β-protons of **2** and **2-d_β** are temperature dependent (Figure 1). Below -80 °C, the chemical shifts of the β-protons of **2** change very little (<0.01 ppm) with temperature, but as the temperature is raised above -80 °C, the resonances move to higher frequencies, while other resonances in the molecules move very little. For example, the resonance observed in the ^{1}H NMR spectrum of **2** at δ -0.17 at -100 °C shifts to δ 0.05 at 5 °C. Furthermore, the chemical shifts of the β-protons of **2** and **2-d_β** are the same above 10 °C; the lack of isotopic perturbation of the chemical shifts indicates that there is no β-agostic interaction at this temperature. These data suggest that the β-agostic complex is in equilibrium with an α-agostic (or perhaps nonagostic) complex, with the less-ordered α-agostic complex favored at higher temperatures (Scheme 3).[17]
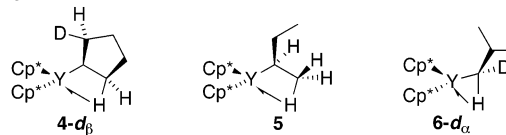
(16) **2-d_β** was synthesized by the reaction of $(Cp*_2YD)_2$ with 3-methyl-1-butene at -50 °C.
(17) The α-agostic interaction in $TpNbCl(i$-Pr$)(MeCCMe)$ is favored by 6.5 eu over the β-agostic interaction: Jaffart, J.; Etienne, M.; Maseras, F.; McGrady, J. E.; Eisenstein, O. *J. Am. Chem. Soc.* **2001**, *123*, 6000.

Scheme 3
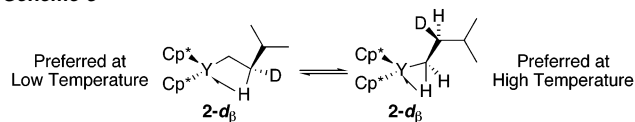
Scheme 4

$Cp*_2YCHR_2$ Complexes Have β-Agostic Interactions. Secondary alkylyttrium complexes also have β-agostic interactions, as shown by the shift of the β-hydrogen resonance of the cyclopentylyttrium complex **4** upon monodeuteration (Scheme 4). Complex **4-d_β** was prepared by reaction of $(Cp*_2YD)_2$ with cyclopentene at -40 °C for 40 min. The IP for deuteration of the β-position is -0.30 ppm at -100 °C. The yttrium in **4** can form an agostic interaction only with the syn protons; consequently, only the syn protons have chemical shifts at lower frequency than the α-proton. Furthermore, the β-CH coupling constant of **4** is 119 Hz, 9 Hz less than that of cyclopentane (128 Hz). Like **2**, **4-d_β** shows a temperature-dependent chemical shift of its β-hydrogen resonance. It moves to higher frequency as the temperature is raised (from δ 0.07 at -100 °C to δ 0.32 at -40 °C), consistent with a shift in the equilibrium away from a β-agostic complex.

The *sec*-butyl complex $Cp*_2YCH(CH_3)CH_2CH_3$ (**5**) also adopts a β-agostic structure, as indicated by the low-frequency resonance for the β-CH_3 protons (δ 0.30). It is noteworthy that the agostic interaction present for the *sec*-butylyttrium complex appears to be that with the methyl group rather than with the ethyl group on the basis of the observation that the methyl protons resonate at lower frequency than the α-proton (δ 0.60), but the CH_2 protons (δ 1.70, 1.78) resonate at higher frequency than the α-proton.

$Cp*_2YCH_2CHR_2$ Complexes Have α-Agostic Interactions. The isobutyl complex $Cp*_2YCH_2CH(CH_3)_2$ (**6**) was synthesized as a simple model for a metal center in a polypropylene polymerization catalyst. Complex **6** (Table 1) has a sterically hindered β-CH and was previously proposed to adopt an α-agostic ground state on the basis of its large $J_{YC} = 51$ Hz and the much higher frequency of its β-hydrogen ^{1}H NMR resonance (δ 1.89) as compared with its α-hydrogen resonance (δ -0.08). However, because the nonagostic complex **6-THF** has similar NMR characteristics, these data for **6** cannot distinguish between an α-agostic interaction and no agostic interaction. To test for the presence of an α-agostic interaction, $Cp*_2YCHDCH(CH_3)_2$ (**6-d_α**) was prepared from the reaction of $(Cp*_2YH)_2$ with $HDC=C(CH_3)_2$. At -60 °C, a substantial isotopic perturbation was seen for the ^{1}H NMR chemical shift α-protons of **6** and **6-d_α** ($\Delta\delta_{IP} = -0.14$ ppm, from δ -0.08 for **6** to -0.22 for **6-d_α**). This convincingly establishes the presence of an α-agostic interaction in **6**. Notably, the chemical shift of the α-proton changes by less than 0.05 ppm upon warming the solution from -90 to -25 °C, indicating that the α-agostic interaction is maintained throughout the temperature range. It is interesting that introduction of a second β-alkyl substituent causes a shift from β-agostic alkylyttrium complexes to α-agostic β-disubstituted alkylyttrium complexes.
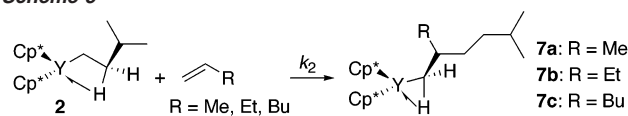
Scheme 5

7a: R = Me
7b: R = Et
7c: R = Bu

Table 2. Rate Constants for Insertion of Alkenes into the Y–C Bonds of Yttrium Alkyls

Cp*$_2$YR	alkene	k_2 (M^{-1} s^{-1})	T (°C)
2	ethylene	rapid	−130
2	propene	15×10^{-4}	−100
2	1-butene	9.2×10^{-4}	−100
2	1-hexene	6.5×10^{-4}	−100
2	3-methyl-1-butene	no insertion	22
14-off	propene	$15(2) \times 10^{-4}$	−100
6	propene	$\sim 0.08 \times 10^{-4}$	−100
6	ethylene	rapid	−130
9	propene	$20(5) \times 10^{-4}$	−103
3	propene	$18(2) \times 10^{-4}$	−103
2	propene	$8(2) \times 10^{-4}$	−103
3	3-methyl-1-butene	decomposition	0

Table 1 summarizes the observation that compounds with β-agostic interactions share three characteristics: (1) β-H resonances appear upfield of α-H resonances, (2) J_{YC} is less than 40 Hz, and (3) C–H coupling constants for β-hydrogens are reduced by ∼10 Hz. The presence of an α-agostic interaction is less obvious than a β-agostic interaction because the coupling constants of an α-agostic complex are the same as those for compounds without any agostic interactions. In these cases, isotopic perturbation of the α-CH resonance provides evidence for an α-agostic interaction. The data further demonstrate that yttrium-alkyl complexes prefer β-agostic interactions if that position is not too sterically congested; sterically crowded complexes prefer α-agostic interactions. Because the alkyl chains of α-agostic complexes have more freedom of motion than those of β-agostic complexes, entropy favors an α-agostic over a β-agostic interaction. Consequently, the equilibrium shifts toward α-agostic complexes as the temperature is raised.

Insertion Chemistry. Having established the ground-state structures of the yttrium alkyls, we next addressed the factors that influence the insertion of alkenes into yttrium alkyl bonds. Watson has studied the insertion of propene into the metal alkyl bond of Cp*$_2$LuMe(L) [L = THF, Et$_2$O, or AlMe$_3$] as a model for alkene insertion in Ziegler−Natta olefin polymerization,[18] but these studies were complicated by the presence of coordinating ligands and an inverse dependence of the rates on ligand concentration. Our studies of insertion of alkenes into yttrium alkyl bonds in the absence of coordinating ligands other than alkenes provide a clearer and more detailed picture of the insertion step in alkene polymerization.
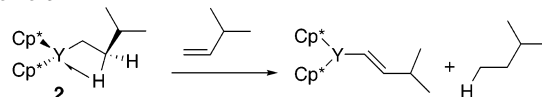
Effect of Alkene Structure on Insertion Rates. The reaction of (Cp*$_2$YH)$_2$ with 3-methyl-1-butene in a 1:1 mixture of methylcyclohexane-d_{14} and pentane-d_{12} proceeded smoothly at −60 °C to give the monoinsertion product Cp*$_2$YCH$_2$CH$_2$CH-(CH$_3$)$_2$ (**2**) in quantitative yield based on the CH$_2$(SiMe$_3$)$_2$ internal standard.[7] While excess 3-methyl-1-butene does not further insert into **2**, less sterically constrained *straight-chain* 1-alkenes insert into the yttrium alkyl bond of **2** at −100 °C over several hours. We have previously determined that the rate law for the reaction of **2** with propene is first-order in both **2** and propene.[5a] To probe the effect of alkene chain length on the rate of insertion into Cp*$_2$YR, we have now compared the rates of insertion of propene, 1-butene, and 1-hexene with **2** (Scheme 5).

When the reaction of **2** with 1-butene at −100 °C was followed by ^{1}H NMR spectroscopy, the resonances [δ 1.89 (Cp*), 0.27 (YCH$_2$), −0.17 (YCH$_2$CH_2)] characteristic of **2** decreased with a concomitant growth of a Cp* resonance at δ 1.92 and alkyl resonances at δ 0.64 (CH$_2$CH_3) and −0.38 (YCH$_2$),[19] assigned to Cp*$_2$YCH$_2$CH(Et)CH$_2$CH$_2$CH(CH$_3$)$_2$ (**7b**). Over several hours, the monoinsertion product **7b** was

Scheme 6

formed quantitatively; further insertion of 1-butene was not observed. Similarly, reaction of **2** with 1-hexene at −100 °C resulted in quantitative formation of the monoinsertion product Cp*$_2$YCH$_2$CH(Bu)CH$_2$CH$_2$CH(CH$_3$)$_2$ (**7c**).

The kinetics of propene, 1-butene, and 1-hexene insertions into the Y−C bond of **2** were monitored under pseudo-first-order conditions of excess alkene at −100 °C (Table 2). The observed rate constant for the reaction of propene (0.12 M) with **2** (0.01 M) was 1.8×10^{-4} s^{-1} ($t_{1/2}$ = 64 min); the second-order rate constant for insertion is $k_2 = 15 \times 10^{-4}$ M^{-1} s^{-1}. Similar kinetic studies gave second-order rate constants for 1-butene and 1-hexene insertions (Table 2). The length of the alkene alkyl chain has only a small effect on the rate of insertion: propene reacts 1.6 times faster than 1-butene and 2.3 times faster than 1-hexene.

The second allylic substituent of 3-methyl-1-butene greatly retards the rate of insertion into **2**. No insertion of 3-methyl-1-butene (0.03 M) into the yttrium alkyl bond of **2** was observed up to 0 °C, where **2** reacted with 3-methyl-1-butene by C−H activation of a vinylic hydrogen (Scheme 6).[20] The rate of this C−H activation reaction (85×10^{-3} M^{-1} s^{-1} at 22 °C) represents an upper limit on the rate of 3-methyl-1-butene *insertion* into the yttrium−carbon bond of **2**. The large barrier for insertion ($\Delta G^\ddagger > 18.7$ kcal mol^{-1}) suggests that a second allylic substituent on an alkene greatly decreases the rate of alkene insertion.

When a solution of **2** was placed under ∼0.2 atm of ethylene at −130 °C, ethylene was rapidly consumed to produce a white polymeric precipitate. Because polymerization was much faster than mass transport of ethylene into solution, it was not possible to estimate either the rate of initiation or the rate of propagation. These rates are expected to be similar.

Effect of Yttrium Alkyl Structure on Insertion Rates. The single-insertion products **7** are the only observed products of the reaction of **2** with 1-alkenes, indicating that the product β-disubstituted yttrium-alkyls **7** are less reactive than the starting γ-substituted yttrium alkyl **2**. To gain insight into this reactivity difference, the model β-disubstituted yttrium-alkyl complex

(18) (a) Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, *212*, 459. (b) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (c) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (d) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

(19) The other resonances are obscured by the pentane-d_{12} and methylcyclohexane-d_{14} solvent mixture.

(20) (a) Casey, C. P.; Tunge, J. A.; Fagan, M. A. *J. Organomet. Chem.* **2002**, *663*, 91. (b) Carr, A. G.; Dawson, D. M.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1999**, *18*, 2933.

Scheme 7

Scheme 8
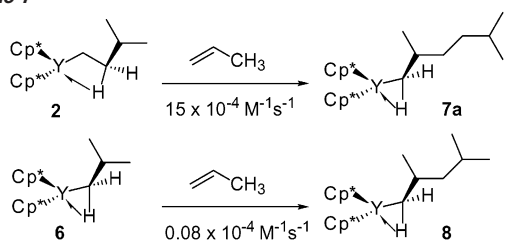
$Cp*_2YCH_2CH(CH_3)_2$ (**6**) was synthesized from the reaction of 2-methylpropene and $(Cp*_2YH)_2$ at $-60\ °C$. In the presence of excess 2-methylpropene, no further insertion to form $Cp*_2$-$YCH_2C(CH_3)_2CH_2CH(CH_3)_2$ was observed up to $0\ °C$, where **6** reacts to form the allyl complex $Cp*_2Y[\eta^3\text{-}CH_2C(CH_3)CH_2]$.[20]

To quantitatively compare the reactivity of **6** and **2** toward propene, the kinetics of the reaction of **6** with excess propene (3.0 M) were measured at $-100\ °C$. ^1H NMR spectroscopy showed that the proton resonances of **6** slowly decreased and resonances grew in at δ 1.89 (Cp*), 0.30 (CH$_3$), and -0.25 (α-CH$_2$). These resonances are tentatively assigned to the new yttrium alkyl complex $Cp*_2YCH_2CH(CH_3)CH_2CH(CH_3)_2$ (**8**) (Scheme 7).[21] At longer reaction times, other products appeared which are presumably higher oligomers. Because of their similar structures, **6** and **8** are expected to react with propene at similar rates. Additionally, at long reaction times, decomposition of **6** is observed, so the kinetics of propene insertion were followed only through the first half-life. The initial rate of disappearance of **6** corresponds to an observed rate constant of 2.4×10^{-5} s^{-1} ($t_{1/2} = 8$ h), giving the second-order rate constant $k_2 = 8 \times 10^{-6}$ M^{-1} s^{-1}.[22] This rate constant for propene insertion into **6** is almost 200 times smaller than the rate constant for propene insertion into **2**, showing that β-disubstitution of the metal alkyl greatly retards the rate of migratory insertion.

Ethylene was rapidly polymerized by **6** at $-130\ °C$, as indicated by the immediate precipitation of a white polymer. Because both **2** and **6** react too rapidly with ethylene to measure kinetics, we were not able to determine whether the β-disubstitution of $Cp*_2YCH_2CH(CH_3)_2$ (**6**) decreases the rate of reaction with ethylene.

To probe the rates of insertion of propene into n-alkylyttrium complexes, we investigated the reaction of $Cp*_2YCH_2CH_2CH_2$-CH_3 (**9**) and $Cp*_2YCH_2(CH_2)_4CH_3$ (**3**) with propene. n-Butyl complex **9** cannot be prepared from $(Cp*_2YH)_2$ and 1-butene because of rapid insertion of 1-butene into **9**. Instead, **9** was prepared in 70–80% yield by treating $(Cp*_2YH)_2$ with *cis*- or *trans*-2-butene at $-50\ °C$; the initially formed 2-butyl complex **5** rearranges to **9** at this temperature. The remaining 20–30% of the yttrium material is the allyl complex $Cp*_2Y(\eta^3\text{-}CH_2\text{-}CHCHCH_3)$.[20] When a solution of **9** and propene was warmed from -130 to $-103\ °C$, the propene insertion product $Cp*_2$-$YCH_2CH(CH_3)(CH_2)_3CH_3$ (**10**) was formed. The second-order rate constant for production of **10** from **9** is $20(5) \times 10^{-4}$ M^{-1} s^{-1}. Similarly, n-hexyl complex **3** was prepared from the reaction of *trans*-3-hexene with $(Cp*_2YH)_2$ at $-30\ °C$ for 5–10 min; this reaction proceeds more smoothly than the reaction with
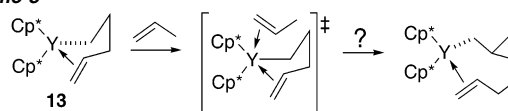
2-butene, and only 1–5% of allyl product $Cp*_2Y(\eta^3\text{-}CH_2\text{-}CHCHBu)$ is formed. Propene (0.22 M) inserts into the Y–C bond of **3** at $-103\ °C$ over several hours ($t_{1/2} = 30$ min) producing $Cp*_2YCH_2CH(CH_3)(CH_2)_5CH_3$ (**11**). The second-order rate constant for the insertion is $18(2) \times 10^{-4}$ M^{-1} s^{-1}. Insertion of propene into the γ-substituted complex **2** under identical conditions occurs with a second-order rate of $8(2) \times 10^{-4}$ M^{-1} s^{-1}, indicating that branching at the γ-position of a metal alkyl slows insertion only about 2-fold.

Alkenes with two or three allylic substituents such as 3-methyl-1-butene and 3,3-dimethyl-1-butene failed to react with **3** or **9** at $-40\ °C$. Complex **3** decomposes in the presence of 3-methyl-1-butene (0.1 M) at $0\ °C$ at an approximate rate of 2×10^{-3} M^{-1} s^{-1}; this places a lower limit on the barrier for insertion of $\Delta G^{\ddagger} \geq 19$ kcal mol^{-1}. This provides another dramatic example that two or three allylic substituents greatly decrease the rate of alkene insertion into carbon–yttrium bonds.

Reaction of Yttrium-Alkyl-Alkene Chelates with Propene. It has been suggested that alkene insertion can be triggered by the coordination of a second alkene to a metal-alkyl-alkene complex.[23] This "trigger model" has been suggested[1b] to account for the observed rate law for propene polymerization by Cp_2-$ZrMe_2$/MAO and the greater than first-order dependence on [propene].[1,3]

We have reported a series of neutral d^0-yttrium-alkyl-alkene chelates as models for intermediates in Ziegler–Natta alkene polymerization.[5b–f] The kinetics of propene insertion into chelated metal-alkyl-alkene complexes should allow us to determine whether insertion can occur through a metal alkyl that has two alkenes coordinated (Scheme 8).

$Cp*_2Y[\eta^1,\eta^2\text{-}CH_2CH_2CH(CH_3)CH{=}CH_2]$ (**12**) and $Cp*_2Y$-$[\eta^1,\eta^2\text{-}CH_2CH_2CH_2CH{=}CH_2]$ (**13**)[24] exist solely as the alkene-bound chelates at all accessible temperatures. There is no reaction of propene (0.3–0.4 M) with either **12** or **13** below $-60\ °C$. This suggests that insertion of propene cannot occur unless the chelated alkene dissociates. The equilibrium constant for alkene dissociation from **13** can be estimated as 4.3×10^{-3} at $-60\ °C$;[25] thus the amount of yttrium alkyl available for reaction with propene is 1 part in 230. The expected first-order rate constant for reaction of propene (0.3 M) with **2** at $-60\ °C$ is 9×10^{-3} s^{-1}.[26] Consequently, the reaction of **13** with propene might be expected to have a rate constant of $(1/230) \times 9 \times 10^{-3}$ s$^{-1} = 4 \times 10^{-5}$ s^{-1} ($t_{1/2} \approx 5$ h). The failure of **13** to react with propene below $-60\ °C$ is consistent with the expected rate of propene reaction with **13** only if the chelated alkene must first dissociate.

(21) The tentative structural assignment of **8** is based on precedent of related reactions. Because the reaction of **6** with propene was used to obtain an upper limit for the rate of propene insertion, rate comparisons do not depend on the accuracy of the structural assignment of **8**.

(22) In addition to alkene insertion, some decomposition was observed, so the rate constant given represents an upper limit of the rate for propene insertion.

(23) (a) Ystenes, M. *J. Catal.* **1991**, *129*, 383. (b) Ystenes, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 71. (c) Munoz-Escalona, A.; Ramos, J.; Cruz, V.; Marinez-Salazar, J. *J. Polym. Sci., Part A* **2000**, *38*, 571. (d) Chien, J. C. W.; Yu, Z.; Marques, M. M.; Flores, J.; Rausch, M. D. *J. Polym. Sci., Part A* **1998**, *36*, 319.

(24) As shown by isotopic scrambling, **13** reversibly inserts the coordinated alkene at $-78\ °C$ to form a strained cyclobutylmethyl compound. The rate of this reversible insertion is much slower ($\Delta G^{\ddagger} = 14.4$ kcal mol^{-1}) than insertion of propene into the alkyl yttrium complex **2**.[5d]
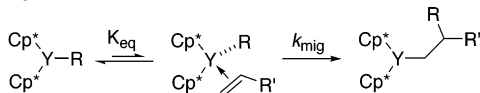
(25) Using $\Delta H° = 4$ kcal mol^{-1} and $\Delta S° = 8$ eu.[5b]

(26) The activation parameters for the reaction of propene with **2** are $\Delta H^{\ddagger} = 5.9(6)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -37(8)$ eu.

Scheme 9
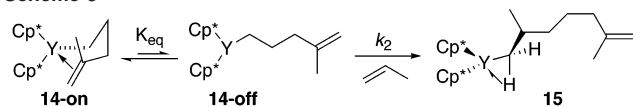
Scheme 10

On the other hand, $Cp*_2Y[CH_2CH_2CH_2C(CH_3)=CH_2]$ (**14**), which exists as a 5:1 equilibrium mixture of alkene-coordinated $Cp*_2Y[\eta^1,\eta^2\text{-}CH_2CH_2CH_2C(CH_3)=CH_2]$ (**14-on**) and uncomplexed $Cp*_2Y[\eta^1\text{-}CH_2CH_2CH_2C(CH_3)=CH_2]$ (**14-off**) at -100 °C, readily reacts with propene (Scheme 9). At -100 °C, the reaction of **14** with propene (0.33 M) is 5–6 times slower (k_{obs} $= 8.9(7) \times 10^{-4}$ s^{-1}, $t_{1/2} = 130$ min) than the reaction of **2** with propene ($t_{1/2} = 23$ min) under identical conditions. Previous work has shown that the equilibrium constant between **14-on** and **14-off** (K_{eq}) is 0.22 and equilibrium is rapidly maintained at -100 °C. A rapid preequilibrium treatment of the mechanism in Scheme 9 gives rate eq 1 for the disappearance of **14**. Using this equation, we determined the second-order rate constant for insertion, $k_2 = 15 \times 10^{-4}$ M^{-1} s^{-1}, using the known values of K_{eq} and [propene]. This rate constant for insertion of propene into **14-off** is (coincidentally) the same value as that measured for propene insertion into $Cp*_2YCH_2CH_2CH(CH_3)_2$ (**2**). At least for these chelates, the "trigger" model for alkene insertion is inoperative.

$$-\frac{d[\mathbf{14}]}{dt} = \frac{k_2 K_{eq}[\mathbf{14}][\text{propene}]}{1 + K_{eq}} \tag{1}$$

Equilibrium Constants for Alkene Binding to Yttrium Alkyls and Kinetic Barriers for Alkyl Migration to a Coordinated Alkene. Having determined the overall rates of alkene insertion into a variety of yttrium alkyls, we wanted to understand the observed differences in reactivity. Why does propene react with $Cp*_2YCH_2CH(CH_3)_2$ (**6**) about 200 times more slowly than with $Cp*_2YCH_2CH_2CH(CH_3)_2$ (**2**)? Is equilibrium binding of propene to **6** much weaker than to **2**, or is the rate of alkyl migration to coordinated alkene much slower? We have shown that the equilibrium for propene binding to an yttrium alkyl can be measured and used to determine the first-order rate constant for alkyl migration to a bound alkene.[5a] Here, we look more closely at alkene binding to a variety of yttrium alkyls, so that the rate constants for alkene insertion (k_2) can be deconvoluted into equilibrium (K_{eq}) and kinetic (k_{mig}) components (Scheme 10). The first step in this process is to measure equilibria for alkene binding to yttrium alkyls.

Dependence of Alkene Complexation Equilibrium on Alkene Structure. The binding of propene, 1-butene, and 1-hexene to $Cp*_2YCH_2CH_2CH(CH_3)_2$ (**2**) was investigated to determine the effect of alkene chain length on binding energy. The barriers to propene coordination and dissociation from **2** have been estimated at 5 kcal mol^{-1}. This means that free and coordinated alkenes are in rapid equilibrium at all accessible temperatures. Thus, the observed chemical shifts are the weighted mean of free and bound alkene. The separation of the chemical shifts ($\Delta\delta = \delta H_Z - \delta H_E$) of the *E*- and *Z*-terminal protons of 1-alkenes is a sensitive probe for alkene binding to

Table 3. Thermodynamics of Alkene Coordination to Yttrium Alkyls and Kinetic Barriers for Alkyl Migration to Coordinated Alkenes

$Cp*_2YR$	alkene	$\Delta G_{-100\,°C}$	$\Delta H°$	$\Delta S°$	$\Delta G_2^{\ddagger}$	$\Delta G_{mig}^{\ddagger}$
2	propene	0.7(6)	$-4.5(3)$	$-30(2)$	12.2	11.5
2	1-butene	1.3(6)	$-3.7(2)$	$-29(2)$	12.3	11.0
2	1-hexene	0.8(7)	$-3.7(2)$	$-26(3)$	12.5	11.7
2	3-methyl-1-butene	≥ 2	≤ 3.2	~ -30	>18.7	
3	propene	0.6(6)	$-4.4(3)$	$-29(2)$	11.9	11.3
6	propene	0.4(6)	$-4.4(3)$	$-28(2)$	14	13.6
4	propene	3.2(7)	$-4.3(2)$	$-29(2)$	≥ 18.6	>15.4

a d^0-metal.[5] The separation of these resonances is small for free alkenes [$\Delta\delta_{free} = 0.06(3)$ ppm], whereas alkenes bound to yttrium exhibit differences in chemical shift of 1.46(6) ppm. Thus, the mole fraction of alkene bound to yttrium can be determined from the observed separation of these resonances using eq 2, where $\Delta\delta_{obs}$ is the observed separation, and $\Delta\delta_{bound}$ is 1.46.[27]

$$\chi_{bound} = \frac{\Delta\delta_{obs} - \Delta\delta_{free}}{\Delta\delta_{bound} - \Delta\delta_{free}} \tag{2}$$

Earlier we communicated the thermodynamics for propene binding to **2** as $\Delta H° = 4.5(3)$ kcal mol^{-1} and $\Delta S° = -30(2)$ eu. In a solution of **2** (0.042 M) and propene (0.02 M) in a 1:1 mixture of pentane-d_{12} and methylcyclohexane-d_{14} at -90 °C, $\Delta\delta_{obs}$ is 0.09 ppm, $\Delta\delta_{free}$ is 0.087 ppm, and $\Delta\delta_{bound}$ is 1.46 ppm corresponding to $>99\%$ free propene. However, when the solution is cooled to -150 °C, $\Delta\delta_{obs}$ increases to 0.76 ppm, indicating that 49% of the propene is bound to yttrium.

Similar, but smaller, changes are observed for solutions of 1-butene or 1-hexene in the presence of **2**. For example, the $\Delta\delta_{obs}$ for 1-hexene (0.013 M) in the presence of **2** (0.025 M) increases from 0.07 ppm at -90 °C to 0.17 ppm at -143 °C, indicating 0 and 7% binding of 1-hexene to **2**. This separation was monitored as a function of temperature to obtain the temperature dependence of K_{eq} and $\Delta H° = -3.7(2)$ kcal mol^{-1} and $\Delta S° = -26(3)$ eu. 1-Butene behaves similarly, giving $\Delta H° = -3.7(2)$ kcal mol^{-1} and $\Delta S° = -29(2)$ eu (Table 3).

No chemical shift changes for either 2-methylpropene or 3-methyl-1-butene were induced by the presence of **2**, indicating that these sterically hindered alkenes are bound much more weakly than the more sterically accessible linear 1-alkenes. For example, $\Delta\delta$ for uncomplexed 3-methyl-1-butene (0.091 ppm) is approximately the same (0.092 ppm) as that for a solution of 3-methyl-1-butene (0.004 M) in the presence of **2** (0.030 M). Assuming $\Delta S° = -30$ eu for alkene binding, $\Delta H°$ for 3-methyl-1-butene binding is calculated to be ≤ 3.2 kcal mol^{-1}.

Dependence of Alkene Complexation Equilibrium on Yttrium Alkyl Structure. Propene binding to **2**, $Cp*_2$-$YCH_2(CH_2)_4CH_3$ (**3**), $Cp*_2YCH_2CH(CH_3)_2$ (**6**), and $Cp*_2Y$-(cyclopentyl) (**4**) was monitored by ^1H NMR spectroscopy. To determine whether **2** is a good model for a straight-chain alkyl complex, its binding of propene was compared to that of the *n*-hexyl complex **3**. For a solution of propene (0.01 M) containing **3** (0.05 M), $\Delta\delta$ was 0.086 ppm at -80 °C, corresponding to $>99\%$ free propene. For the same solution at -140 °C, $\Delta\delta$ was 0.39 ppm, indicating that 22% of the propene

(27) Thermodynamic determinations using separations ($\Delta\delta_{bound}$) of 1.2 or 1.6 ppm ultimately led to small variations in ΔH and ΔS of 0.1 kcal mol^{-1} and 1 eu, respectively.
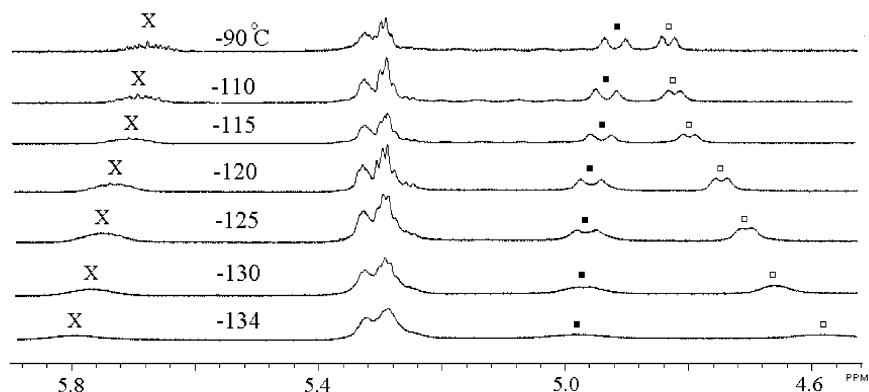
Figure 2. Chemical shifts of propene in the presence of *n*-hexylyttrium complex **3**. X = H_{int}, ■ = H_Z, □ = H_E. Unmarked resonances are 2- and 3-hexene.

Scheme 11
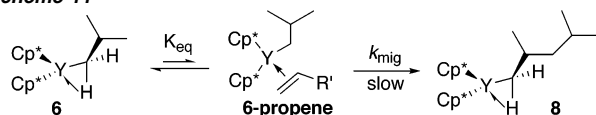
was bound to yttrium (Figure 2). Analysis of the temperature dependence of the equilibrium constant gives $\Delta H° = -4.4(3)$ kcal mol^{-1} and $\Delta S° = -29(2)$ eu for binding of propene to **3**.

The isobutyl complex **6** is the simplest model of an yttrium with a growing polypropylene chain. Complex **6** inserts propene about 200 times slower than does **2**, indicating that the isobutyl group is either a poor migrating group or it interferes with propene binding to yttrium. The binding of propene to isobutyl complex **6** was investigated by NMR spectroscopy at low temperatures. For a solution of propene (0.0144 M) containing **6** (0.022 M), $\Delta\delta$ was 0.12 at -118 °C and 0.42 at -143 °C, corresponding to 2 and 24% propene binding, respectively. A van't Hoff plot showed that thermodynamics of propene binding to **6** [$\Delta H° = -4.4(3)$ kcal mol^{-1} and $\Delta S° = -28(2)$ eu] were similar to those for propene binding to **2**. Using these thermodynamic parameters, we calculated the ratio of **6**:**6-propene** to be 2:1 under the conditions used to monitor propene insertion into **6** at -100 °C and 3.0 M propene. The observation that the equilibrium for propene binding to **2** and **6** is similar suggests that the about 200-fold rate difference for insertion of propene is due to a high kinetic barrier for migration of the isobutyl ligand to coordinated propene (Scheme 11).

Secondary Yttrium-alkyls as Models for 2,1-Misinsertions. Secondary alkyl complexes of Zr are important in metallocene-catalyzed propene polymerization because 2,1-misinsertions of propene have been proposed to result in catalyst deactivation.[1] Propene is proposed to insert very slowly into the secondary alkyl−Zr bond. This ties the catalyst up in a dormant form, and the active form can only be regenerated by β-hydride elimination. To directly address the reactivity of secondary alkylmetal complexes toward alkenes, we sought to exploit our ability to use model yttrium complexes to monitor binding and insertion of alkenes. Our goal was to determine whether the low reactivity of secondary alkyl-metal complexes is due to poor alkene binding or kinetically slow alkyl migration to a coordinated alkene. The cyclopentyl complex **4** was prepared as a model for the product of a 2,1-misinsertion of propene. The temperature-dependent ^{1}H NMR spectra of propene (0.018 M) in the presence of **4** (0.056 M) were nearly identical to those of the propene in the presence of **2**. The thermodynamic parameters for alkene binding are $\Delta H° = -4.3(2)$ kcal mol^{-1} and $\Delta S° =$

Scheme 12
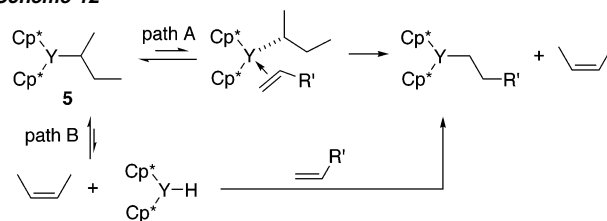
$-29(2)$ eu. This result shows that propene binds well to **4**; yet there was no evidence for propene insertion into the cyclopentyl bond up to -15 °C where β-hydride elimination takes place. The yttrium hydride is rapidly trapped by reaction with propene that produces Cp*$_2$YCH$_2$CH(CH$_3$)CH$_2$CH$_2$CH$_3$ (**16**). These experiments demonstrate that secondary alkyls insert alkenes slowly not because they bind alkenes too weakly, but because the secondary alkyl migrates to coordinated alkene so slowly.

As mentioned above, a regioerror in propene insertion results in a secondary alkyl-metal complex that does not undergo further propene insertion. Two chain-transfer pathways have been suggested for regeneration of the active catalyst from the secondary alkyl complex: (A) direct transfer of a β-hydrogen to a bound alkene and (B) β-hydride elimination followed by insertion of an alkene into the resulting M−H bond (Scheme 12). In principle, the two pathways can be distinguished by the dependence of the chain-transfer rate on alkene concentration. β-Hydride to monomer (path A) transfer will be first-order in alkene, whereas (assuming alkene insertion into the metal hydride is fast) path B will have a zero-order dependence on alkene.[28]

The *sec*-butyl complex **5** was used as a model for the product of 2,1-misinsertion. β-Hydride elimination from this complex will produce Cp*$_2$YH and either 1-butene or 2-butene. We reasoned that the Cp*$_2$YH formed could be trapped by a reactive alkene present in large excess. This overall process would be akin to chain transfer. Indeed, **5** and 3-methyl-1-butene reacted at -60 °C to produce Cp*$_2$YCH$_2$CH$_2$CH(CH$_3$)$_2$ (**2**) in quantitative yield (Scheme 13). 2-Butene was the only byproduct; no 1-butene was observed. This is intriguing because the *sec*-butyl complex **5** has a β-agostic interaction with the methyl hydrogen and not with the ethyl hydrogen that is eliminated. Similarly, **5** and propene reacted at -60 °C to form Cp*$_2$YCH$_2$CH(CH$_3$)CH$_2$-CH$_2$CH$_3$ (**16**) in >95% yield.

(28) A thorough kinetic analysis shows that the rate of alkene liberation by β-hydride to metal elimination can have an apparent first-order dependence on [alkene] if formation of the secondary alkyl is rate-limiting: Liu, Z.; Somsook, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 11193.

Scheme 13
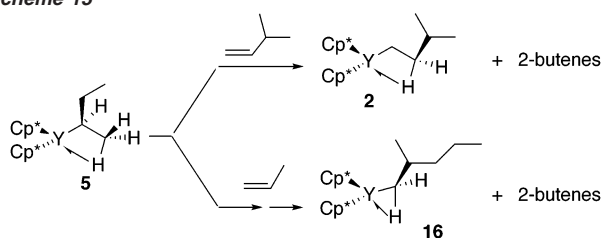
To determine whether chain-transfer mechanism A or B was dominant for yttrium alkyls, the rate of disappearance of **5** was monitored by ^{1}H NMR spectroscopy at two different alkene concentrations. At -78 °C, the rate of disappearance of **5** was $4.6(5) \times 10^{-4}$ s^{-1} at 0.14 M propene and $5.5(5) \times 10^{-4}$ s^{-1} at 2.04 M propene [$\Delta G^{\ddagger} = 14.2$ kcal mol^{-1}]. The rate of disappearance of **5** did not vary significantly over an >10-fold variation in propene concentration. The zero-order dependence on propene concentration is consistent with chain transfer occurring by path B involving β-hydride elimination to form Cp*$_2$YH, followed by insertion of a different alkene into the metal−hydride bond. Furthermore, the barrier for chain transfer from **5** (14.2 kcal mol^{-1}) is lower than the barrier expected for 2,1-insertion of propene.[29] Therefore, it seems likely that the rate-limiting step for vinylene formation with yttrium catalysts will be insertion and not β-hydride elimination.

In contrast to the *sec*-butyl complex **5**, which liberates 2-butene at -80 °C, the *n*-butyl complex **9** ($\sim$0.025 M) does not react with excess 3-methyl-1-butene (0.11 M) to liberate 1-butene (or 2-butene) even at -15 °C. There are several possible explanations for the failure of **9** to react with 3-methyl-1-butene. First, **9** may not β-hydride eliminate at -15 °C. Second, a Cp*$_2$YH(1-butene) complex might form reversibly, but not dissociate 1-butene. Third, Cp*$_2$YH and free 1-butene might form, but the Cp*$_2$YH may re-add 1-butene much faster than it reacts with 3-methyl-1-butene, so only **9** is observed.

To test this third possibility, (Cp*$_2$YH)$_2$ (0.07 M) was allowed to react with a 2:1 mixture of 3-methyl-1-butene (0.27 M) and propene (0.29 M). Cp*$_2$YCH$_2$CH(CH$_3$)CH$_2$CH$_2$CH(CH$_3$)$_2$ (**7a**) and Cp*$_2$YCH$_2$CH(CH$_3$)CH$_2$CH$_2$CH$_3$ (**16**) formed in a 1:1 ratio. Complex **7a** is the product of the reaction of 3-methyl-1-butene with Cp*$_2$YH forming Cp*$_2$YCH$_2$CH$_2$CH(CH$_3$)$_2$ (**2**), which then reacts with propene. Similarly, **16** is formed by reacting propene with Cp*$_2$YH, followed by insertion of another molecule of propene. The fact that the products form in equal quantities indicates that Cp*$_2$YH reacts only $\sim$1.5 times faster with propene than with 3-methyl-1-butene.[30] This experiment shows that if free 1-butene were being formed by β-hydride elimination from **9**, it would have been observed along with Cp*$_2$YCH$_2$-CH$_2$CH(CH$_3$)$_2$. Therefore, either β-hydride elimination does not occur at all or it occurs to reversibly form Cp*$_2$YH(1-butene), which does not dissociate 1-butene.

The observation that Cp*$_2$YH reacts nearly as fast with 3-methyl-1-butene as it does with propene is surprising considering that Cp*$_2$YCH$_2$CH$_2$CH(CH$_3$)$_2$ (**2**) reacts with propene

at -100 °C, but does not insert 3-methyl-1-butene even at 25 °C. Thus, while the reactivity of yttrium alkyls toward alkenes depends strongly on the structure of the alkene, the reactivity of yttrium hydride toward alkenes shows much less structural dependence.

Although β-hydride elimination from **9** has not been directly observed, there is evidence that related compounds undergo β-hydride elimination. When a solution of **2-d_β** was warmed to -5 °C, the rapid growth ($t_{1/2} \approx 5-10$ min) of a resonance at δ 5.72 in the ^{2}H NMR spectrum was observed. This resonance is due to H$_2$C=CDCH(CH$_3$)$_2$, presumably formed by β-hydride elimination. Therefore, it is likely that *n*-butyl complex **9** is undergoing reversible formation of Cp*$_2$YH(1-butene) at similar temperatures, but does not dissociate 1-butene. A corollary is that when 1-butene coordinates to Cp*$_2$YH, it is irreversibly committed to formation of the *n*-butyl complex **9**.

Stereochemical Inversion at Yttrium. Stereochemical inversion at the metal center is an important process in the syndiospecific polymerization of alkenes by metallocene catalysts. The syndiospecificity observed for Ewen's C_s symmetric catalyst requires inversion at the metal center accompanying each monomer insertion and no inversion between insertions (Scheme 14). If site epimerization (the combination of rotation about the Zr−C bond and inversion of stereochemistry at zirconium) were competitive with insertion, many stereoerrors would have resulted.

Site epimerization at yttrium was addressed using Cp*$_2$YCH-(CH$_3$)CH$_2$CH$_3$ (**5**). The ^{1}H NMR spectrum of **5** at -90 °C showed two resonances for the diastereotopic Cp* ligands. Upon warming the solution, we found that these resonances broadened and eventually coalesced near -43 °C ($\Delta G^{\ddagger} = 11.4$ kcal mol^{-1}).[31] The temperature-dependent line-broadening of the Cp* ligands of **5** gave activation parameters for site epimerization at yttrium: $\Delta H^{\ddagger} = 10.9(4)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0(2)$ eu. Site epimerization interconverts the diastereotopic Cp* resonances of **5** and requires both inversion of stereochemistry at yttrium and 180° rotation about the Y−C bond (Scheme 15).

We previously measured a barrier of 7 kcal mol^{-1} for site epimerization of the primary alkylyttrium complex Cp*$_2$YCH$_2$-CH$_2$CH(CH$_3$)CH=CH$_2$ (**12-off**). The much higher barrier for site epimerization of a secondary alkyl (10.9 kcal mol^{-1}) is consistent with rate-limiting rotation about the secondary C−Y bond in the case of *sec*-butyl complex **5**. (The lower barrier for the primary alkyl **12-off** might be due to either inversion at Y or rotation about the primary C−Y bond.) Slow rotation about the C−Y bond was also observed for Cp*$_2$YCH(SiMe$_3$)$_2$, which exhibits a single TMS resonance and two Cp* resonances between -130 and 90 °C, indicating that rotation is always slow ($\Delta G_{\text{rot}}^{\ddagger} > 19$ kcal mol^{-1}) and inversion is always fast ($\Delta G_{\text{inv}}^{\ddagger} \leq 7.5$ kcal mol^{-1}).

We attempted to observe an interchange of the environments of the diastereotopic Cp* ligands of the cyclopentylyttrium complex **4**, which requires only 120° rotation about the Y−C bond, but not inversion at yttrium (Scheme 15). However, only a single Cp* resonance was observed in the ^{1}H NMR spectrum of **6** at -100 °C. This is consistent with accidental degeneracy

(29) 2,1-insertion is known to have a much larger barrier than 1,2-insertion ($\sim$13.5 kcal mol^{-1}) of propene into the growing polymer. The $\Delta H^{\ddagger}$ for 2,1-insertion is 3.3 kcal mol^{-1} higher than that for 1,2-insertion with [*rac*-(C$_2$H$_4$(1-indenyl)$_2$)ZrMe][MeB(C$_6$F$_5$)$_3$].[27]

(30) We cannot tell the exact reactivity ratio from this experiment because the concentration of propene changes at a different rate than the concentration of 3-methyl-1-butene.
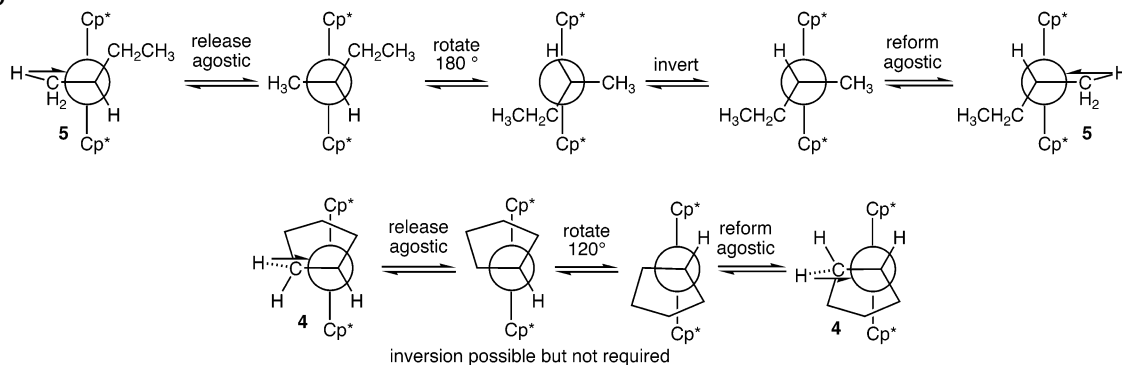
(31) The exact coalescence temperature was difficult to discern because substantial quantities of **9** formed by isomerization of **5** prevented proper determination.
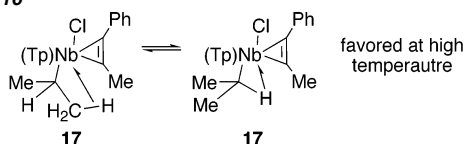
Scheme 14
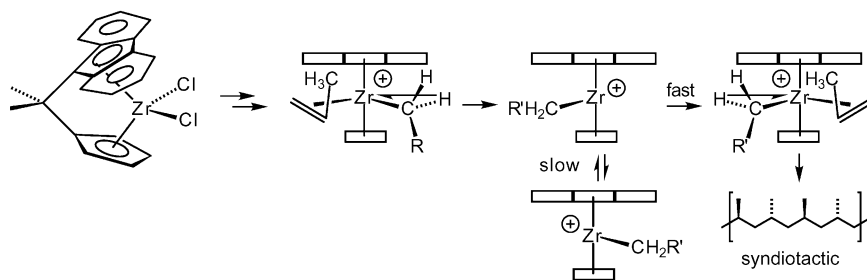
Scheme 15

Scheme 16

of the Cp* chemical shifts, but we cannot exclude the possibility that 120° rotation about the Y−C bond is fast on the NMR time scale.

Discussion

The ground-state structures of d^0-yttrocene alkyl complexes have agostic interactions of CH bonds with the electron-deficient yttrium center. Our data indicate that the β-CH$_2$ agostic interaction in primary alkyls is stronger than the α-CH$_2$ interaction. For secondary alkyls, the order of strengths of agostic interactions is β-CH$_3 > \beta$-CH$_2 > \alpha$-CH. Interestingly, the observed temperature-dependent chemical shifts of Cp*$_2$-YCH$_2$CH$_2$CH(CH$_3$)$_2$ (**2**) indicate that the β-CH$_2$ agostic interaction is replaced by an α-CH$_2$ agostic interaction (or no agostic interaction) as the temperature is increased. Similar temperature-dependent behavior was observed by Jaffart for the trispyrazolylborate (Tp) niobium complex **17**, which exists as an equilibrium mixture of α- and β-agostic structures; the α-agostic complex is entropically favored by 6.5 eu (Scheme 16).[17]

The steric bulk of two β-alkyl substituents in complexes such as Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (**6**) destabilizes β-agostic interactions and causes a shift to a ground-state structure with an α-CH$_2$ agostic interaction. The steric dependence of agostic interactions was also observed by Jordan who reported that Cp*$_2$HfCH$_2$-CH(CH$_3$)$_2$(PMe$_3$)$^+$ has an α-agostic interaction, whereas the sterically smaller complex (C$_5$H$_4$Me)$_2$HfCH$_2$CH(CH$_3$)$_2$(PMe$_3$)$^+$ has a β-agostic interaction.[32] Steric inhibition of β-agostic interactions may be a root cause of why propene polymerizations using bulky metallocenes (Cp*$_2$ZrR$^+$) terminate primarily by

(32) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424.

β-methyl elimination rather than β-hydride elimination.[33] The inaccessibility of the β-hydrogen in the sterically crowded Cp*$_2$-ZrCH$_2$CH(CH$_3$)Pol$^+$ may prevent β-hydride elimination, while the greater steric accessibility of a β-methyl group allows β-methyl elimination. Similarly, we have observed β-methyl elimination from the α-agostic complex Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (**6**) at 0 °C.[18,20]

The equilibrium constants and thermodynamics of alkene binding to the primary alkyl yttrium complex Cp*$_2$YCH$_2$CH$_2$-CH(CH$_3$)$_2$ (**2**) depend strongly on the structure of the alkene. A single allylic substituent on the alkene has a small effect on alkene binding, but a second allylic substituent has a large destabilizing effect. Thus, alkene binding to **2** falls in the order propene > 1-butene $\approx$ 1-hexene $\gg$ 3-methyl-1-butene, 2-methylpropene.

The rates of insertion of *n*-alkenes into yttrocene alkyl bonds do not depend on the chain length of the inserting alkene, but no insertion is seen for alkenes with two (3-methyl-1-butene) or three (3-methyl-1-butene) allylic alkene substituents. This reactivity order parallels the observed binding abilities of the alkenes.

Surprisingly, the propene binding to yttrium alkyls is largely independent of the nature of the alkyl ligand. Equilibrium constants for propene binding to *n*-, γ-substituted, β-substituted, and secondary alkyl yttrium complexes are essentially the same. However, this does not require that the binding energy of propene to each of the hypothetical nonagostic alkyls is the same. Alkene binding can be thought of as a two-step process proceeding via a hypothetical nonagostic alkyl intermediate. Each of the metal alkyl complexes has a different ground-state agostic interaction that is likely to be lost upon alkene complexation. The γ- and *n*-substituted complexes **2** and **3** have

(33) (a) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (b) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (c) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277.

Scheme 17

Scheme 18

Scheme 19

Scheme 20
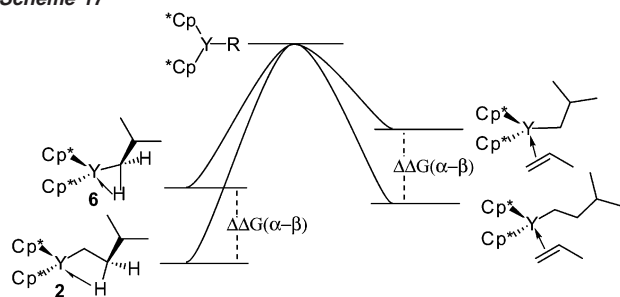
β-agostic interactions that are stronger than either the α-agostic interaction in the β-substituted complex **6** or the β-agostic interaction in the cyclopentyl complex **4**. The less crowded hypothetical nonagostic complexes related to **2** and **3** would be expected to bind propene more strongly than the more crowded nonagostic complexes **4** and **6**. The breaking of a stronger agostic interaction is compensated for by stronger binding of propene to the hypothetical nonagostic alkyl. The net result is that propene binding is insensitive to the nature of the yttrium alkyl (Scheme 17).

In contrast, the nature of the alkyl group on yttrium has a large dominant effect on the rates of migratory insertion. While *n*-alkylyttrium complex **3** and γ-substituted alkylyttrium complex **2** have a barrier for alkyl migration to coordinated propene of $11-11.5$ kcal mol^{-1}, the isobutylyttrium complex **6** has a significantly higher barrier of $\sim$13.6 kcal mol^{-1} for alkyl migration to coordinated propene. The barrier for migration of the cyclopentyl ligand of **4** could only be estimated as $>$15.4 kcal mol^{-1}. Thus, the ability of an alkyl group on yttrium to migrate to coordinated propene is *n*-alkyl $\approx$ γ-substituted $\gg$ β-substituted $\gg$ α-substituted.

Branching at the β-position of the yttrium-alkyl chain greatly retards reaction with alkenes. The second-order rate constant for propene insertion into Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (**6**) is $\sim$200 times smaller than that for insertion into Cp*$_2$YCH$_2$CH$_2$CH-(CH$_3$)$_2$ (**2**). This is one factor that helps to explain why yttrocene-catalyzed polymerization of propene, which produces a β-branched yttrium alkyl complex Cp*$_2$YCH$_2$CH(CH$_3$)R, is much slower than the polymerization of ethylene, which produces *n*-alkylyttrium complexes Cp*$_2$YCH$_2$CH$_2$R. Other factors that we have not been able to experimentally verify because of the extremely high reactivity of ethylene are that ethylene is expected to bind to yttrium more strongly than propene and the rate of alkyl migration to coordinated ethylene is likely to be faster than that to coordinated propene.

The fact that the β-branched complex Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (**6**) binds propene as well as Cp*$_2$YCH$_2$CH$_2$CH(CH$_3$)$_2$ (**2**) leads to the surprising conclusion that the 200-fold difference in reactivity between **2** and **6** is due to a slower rate of migration of the isobutyl group to propene. The origin of the kinetic barrier to migration of the isobutyl ligand is not well understood. We are considering two possibilities that differ in whether the transition state for alkyl migration to coordinated alkene has an α- or β-agostic interaction. Ziegler has carried out computational studies for two different mechanisms for ethylene insertion into the Y−C bonds of (H$_2$N)$_2$YCH$_2$CH$_3$ and (HO)$_2$-YCH$_2$CH$_3$.[9] The two mechanisms are differentiated by whether the entrance channel of the alkene is on the "front-side" or "back-side" of the β-agostic interaction in the reacting yttrium
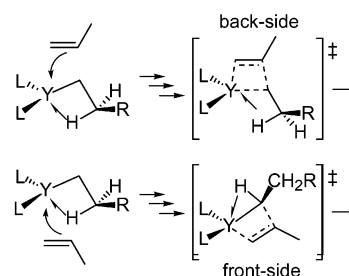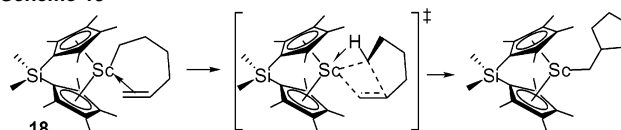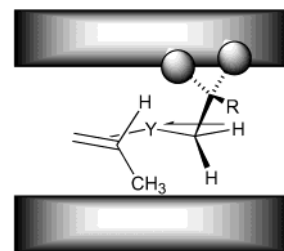
alkyl (Scheme 18). The "front-side" approach leads to a transition state stabilized by an α-agostic interaction, while the "back-side" approach leads to a transition state stabilized by a β-agostic interaction. Ziegler also notes that group 3 complexes, which easily adopt trigonal geometries, are more likely than their group 4 analogues to undergo back-side insertion involving a β-agostic interaction.

The more rapid reaction of propene with **2** than with **6** can be readily explained in terms of a "back-side" approach of propene and a transition state stabilized by a β-agostic interaction. Complex **2**, which has a ground-state β-agostic interaction, inserts propene rapidly, while isobutyl complex **6**, which has a reduced ability to form a β-agostic interaction and has a ground-state α-agostic interaction, inserts propene more slowly.

Alkene insertion mechanisms involving a transition state in which an α-agostic alkyl group migrates to a coordinated alkene have been proposed and are supported by isotope effect measurements.[34] For example, Bercaw has shown that Sc complex **18** undergoes insertion through an α-agostic-stabilized transition state (Scheme 19).[35,36] Therefore, it is possible that yttrium alkyls also insert alkenes with α-agostic assistance. While a single β-alkyl substituent on the migrating α-agostic alkyl group can be easily directed away from the metal center, the presence of a second β-alkyl substituent on the migrating alkyl might encounter severe steric interactions with a Cp* ligand (Scheme 20).

In contrast to Cp$_2$ZrR$^+$ alkene polymerization catalysts, Cp*$_2$-YR complexes polymerize ethylene, but not propene. Given the low barriers for insertion of propene into yttrocene alkyls, it

(34) (a) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 7, 1651. (b) Cotter, W. D.; Bercaw, J. E. *J. Organomet. Chem.* **1991**, *417*, C1. (c) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412.
(35) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406.
(36) Consideration of the geometric requirements for this intramolecular cyclization indicates that only the "front-side" transition state is accessible.

might be expected that yttrium alkyls would be good propene polymerization catalysts. However, termination pathways such as β-CH$_3$ elimination, β-hydride elimination, and C−H activation are also facile for yttrocenes and limit their ability to produce polymer.[37] We have previously shown that, in the oligomerization of propene by Cp*$_2$YCH$_2$CH(CH$_3$)R, the barrier for propagation is approximately equal to the barrier for C−H activation to form inactive Cp*$_2$Y(η^3-CH$_2$CHCH$_2$).[20]

Experimental Section

Cp*$_2$YCH$_2$CH$_2$CH(CH$_3$)CH$_2$CH$_3$ (1). 3-Methyl-1-pentene (0.054 mol) was condensed into an NMR tube containing (Cp*$_2$YH)$_2$ (0.021 mmol) in methylcyclohexane-d_{14} (0.44 mL) at −196 °C. The tube was shaken intermittently at −78 °C, producing a pale-yellow solution of **1** (95 ± 5% yield based on CH$_2$TMS$_2$ internal standard). Complex **1** was stable below −30 °C and was analyzed without isolation. ^{1}H NMR (500 MHz, −80 °C, C$_6$D$_{11}$CD$_3$): δ 1.90 (s, C$_5$Me$_5$), 1.89 (CH, partially obscured by Cp*), 1.54 (br m, C*H*HCH$_3$), 1.44 (m, CH*H*CH$_3$), 0.91 (t, J = 7.5 Hz, CH$_2$C*H*$_3$), 0.81 (br d, J = 7 Hz, CHC*H*$_3$), 0.25 (br m, YCH$_2$), −0.04 (br m, YCH$_2$C*H*H), −0.19 (br m, YCH$_2$CH*H*). ^{13}C NMR (125.7 MHz, −80 °C, C$_6$D$_{11}$CD$_3$): δ 116.5 (C$_5$Me$_5$), 45.6 (t, J_{CH} = 109.1 Hz, YCH$_2$CH$_2$), 40.7 (d, J_{CH} = 127.0 Hz, CH), 38.5 (td, J_{CH} = 125.0 Hz, J_{YC} = 35.1 Hz, YCH$_2$), 30.5 (t, J_{CH} = 122.2 Hz, C*H*$_2$CH$_3$), 20.0 (q, J_{CH} = 125.9, CHCH$_3$), 11.7 (q, J_{CH} = 126.0 Hz, CH$_2$CH$_3$), 10.8 (q, J_{CH} = 126.0 Hz, C$_5$Me$_5$).

Cp*$_2$YCHCH$_2$CH$_2$CH$_2$CH$_2$ (4). Cyclopentene (0.090 mmol) was measured using a monometer and added to (Cp*$_2$YH)$_2$ (11 μmol in 400 μL of methylcyclohexane-d_{14}) at −196 °C. This mixture was warmed to −40 °C and shaken to give a solution of **4** (80−95% yield based on CH$_2$(SiMe$_3$)$_2$ internal standard). ^{1}H NMR (500 MHz, −60 °C, C$_6$D$_{11}$CD$_3$): δ 1.88 (s, C$_5$Me$_5$), 1.80 (m, β-C*H*H), 1.79 (m, γ-C*H*H), 1.50 (m, γ-CH*H*), 1.00 (m, ↔ 1.8, YCH), 0.50 (m, ↔ 1.0, ↔ 1.5, ↔ 1.8, β-CH*H*). ^{13}C{^{1}H} NMR (125.7 MHz, −60 °C, C$_6$D$_{11}$CD$_3$): δ 116.04 (s, C$_5$Me$_5$), 53.05 (d, J_{YH} = 39.7 Hz, YCH), 35.66 (↔ 0.50, ↔ 1.80, β-CH$_2$), 29.16 (↔ 1.50, ↔ 1.79, γ-CH$_2$), 10.85 (C$_5$(CH$_3$)$_5$). 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 ↔.

Cp*$_2$YCH(CH$_3$)CH$_2$CH$_3$ (5). We have previously described the preparation of **5** from (Cp*$_2$YH)$_2$ and *cis*- or *trans*-2-butene. Complex **5** was produced in varying quantities along with **9**, the product of isomerization. Now we have found that **5** can be prepared in greater overall purity using (Cp*$_2$YH)$_2$ produced from samples of Cp*$_2$YCH-[Si(CH$_3$)$_2$]$_2$ that were not recrystallized. Evidently, a small amount of residual THF accelerates insertion of alkenes, while isomerization is unaffected.[38] ^{1}H NMR (500 MHz, −60 °C, C$_6$D$_{11}$CD$_3$): δ 0.32 (d, $^3J_{HH}$ = 8.0 Hz, ↔ 0.68, YCHC*H*$_3$), 0.68 (br, ↔ 0.32, ↔ 1.68, YCH), 0.76 (m, ↔ 1.68, ↔ 1.78, CH$_2$C*H*$_3$), 1.68 (m, ↔ 0.76, ↔ 0.68, C*H*HCH$_3$), 1.78 (m, ↔ 0.76, CH*H*CH$_3$), 1.86 (C$_5$(CH$_3$)$_5$), 1.89 (C$_5$(CH$_3$)$_5$). ^{13}C-{^{1}H} NMR (90 MHz, −60 °C, C$_6$D$_{11}$CD$_3$): δ 17.13 (↔ 0.76, CH$_2$CH$_3$), 23.64 (↔ 0.32, YCHCH$_3$), 28.62 (↔ 1.68, ↔ 1.78, CH$_2$), 44.88 (d, J_{YC} = 36 Hz, ↔ 0.68, YCH). 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 ↔.

Kinetics of Propene Insertion into the Y−C Bond of Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (6). Cp*$_2$YCH$_2$CH(CH$_3$)$_2$ (**6**) (0.02 mmol) was prepared by the reaction of isobutylene with (Cp*$_2$YH)$_2$ in a mixture of methylcyclohexane-d_{14} (0.34 mL) and pentane-d_{12} (0.17 mL) as previously described.[5a] Propene (500 mm, 3.04 M) was condensed into the solution at −196 °C. The solution was shaken at −130 °C, and then warmed to −100 °C in the NMR probe. The disappearance of **6** was monitored by following the decrease in the ^{1}H NMR resonances at δ 1.92 (Cp*) and 0.67 (d, $^3J_{HH}$ = 6.5, CH(C*H*$_3$)$_2$). Initially, a single product formed that we tentatively assign as Cp*$_2$YCH$_2$CH(CH$_3$)-CH$_2$CH(CH$_3$)$_2$ (**8**). Because of its transient nature, we were only able to obtain partial ^{1}H NMR characterization of **8** by TOCSY 1D NMR. ^{1}H NMR (500 MHz, −60 °C, C$_6$D$_{11}$CD$_3$): δ 1.88 (s, C$_5$Me$_5$), 1.68 (↔ 0.29, ↔ −0.24, YCH$_2$C*H*), 1.05 (m), 0.87 (d, J = 6.7 Hz, CH(C*H*$_3$)$_2$), 0.29 (br d, J ≈ 6 Hz, ↔ 1.68, YCH$_2$CH(C*H*$_3$)), −0.24 (m, YCH$_2$).

Supporting Information Available: Experimental procedures, spectroscopic data, and kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(37) Clever catalyst design can inhibit the C−H activation process, making it possible to polymerize propene with yttrocene catalysts: (a) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. (b) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606.

(38) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161.

JA0209971