Alkyl Rearrangement Processes in Organozirconium Complexes. Observation of Internal Alkyl Complexes during Hydrozirconation

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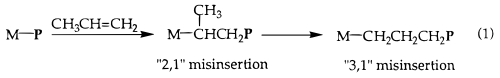
Abstract: Isotopically labeled alkyl zirconocene complexes of the form $(CpR_n)_2Zr(CH_2CDR'_2)(X)$ (CpR_n = alkyl-substituted cyclopentadienyl; R′ = H, alkyl group; X = H, D, Me) undergo isomerization of the alkyl ligand as well as exchange with free olefin in solution under ambient conditions. Increasing the substitution on the Cp ring results in slower isomerization reactions, but these steric effects are small. In contrast, changing X has a very large effect on the rate of isomerization. Pure σ-bonding ligands such as methyl and hydride promote rapid isomerization, whereas π-donor ligands inhibit β-H elimination and hence alkyl isomerization. For $(\eta^5\text{-}C_5H_5)_2Zr(R)(Cl)$, internal alkyl complexes have been observed for the first time. The rate of isomerization depends on the length of the alkyl group: longer alkyl chains (heptyl, hexyl) isomerize faster than shorter chains (butyl). The transient intermediate species have been identified by a combination of isotopic labeling and ^1H, ^2H, and ^{13}C NMR experiments. The solid-state structure of the zirconocene cyclopentyl chloride complex, $Cp_2Zr(cyclo\text{-}C_5H_9)(Cl)$, has been determined by X-ray diffraction.

Introduction

Alkyl complexes play a central role in organotransition metal chemistry in both catalytic and stoichiometric transformations.[1] The preferences (kinetic and/or thermodynamic) of a transition metal to bond to a terminal or an internal carbon atom of an alkyl ligand often determine the selectivity and productivity of a system. However, delineation of the factors that govern these preferences is by no means straightforward. The identities of the transition metal, coordination environment, and ancillary ligation all influence the relative stabilities for terminal versus internal alkyl complexes.[2]

Alkyl isomerization has special relevance, both historical and practical, in group 4 metallocene chemistry. The original studies by Schwartz and co-workers[3] reported the hydrozirconation of internal olefins with $[Cp_2Zr(H)(Cl)]_n$ as yielding solely terminal products. This hydrometalation−isomerization protocol allows for functionalization of otherwise unactivated methyl groups and has found widespread synthetic utility.[4]

More recently, alkyl isomerization reactions have been found to influence the stereo- and regiochemical outcome of group 4 metallocene-catalyzed olefin polymerizations.[5] The degree of isotacticity of the polypropylene produced from a variety of C_2-symmetric zirconocene catalysts has been shown to decrease with decreasing monomer concentration.[6] The explanation for this behavior is an alkyl isomerization process that competes with olefin insertion at low monomer concentrations. Isomerization of a "2,1"-inserted monomer unit producing a "3,1"-regiomistake has also been identified (eq 1).[7] Despite efforts to suppress both of these pathways, the origins of alkyl isomerization and the identities of the mechanisms and their rate-limiting steps have remained elusive.



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In this report we describe direct observation of the alkyl isomerization process in several neutral zirconocene complexes of the form $(CpR_n)_2Zr(CH_2CHR'_2)(X)$ (X = H, Me, Cl; CpR_n = alkyl-substituted η^5-cyclopentadienyl; R′ = H or alkyl). Factors that affect the facility of the isomerization process are disclosed. Additionally, evidence for involvement of free olefin in the mechanism of alkyl isomerization is presented.

Results

Rearrangement of Labeled Alkyls Obtained from Hydrozirconation of Terminal Olefins. Zirconocene alkyl hydride complexes are prepared via addition of the appropriate olefin to the zirconocene dihydride.[8,9] This synthetic protocol allows facile incorporation of isotopic labels into the zirconocene alkyl

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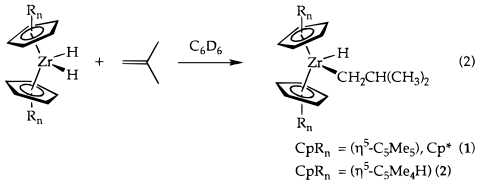
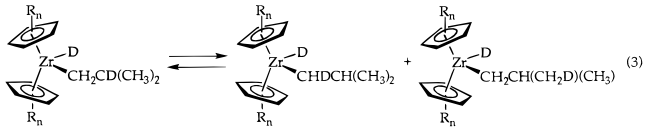
hydride complex (eq 2). Thus, reaction of substituted zir-



(2)

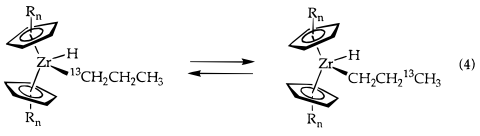
conocene dideuterides, $(CpR_n)_2ZrD_2$ ($CpR_n = (\eta^5\text{-}C_5Me_5)$ (Cp*), $(\eta^5\text{-}C_5Me_4H)$), with isobutylene in benzene solution affords specifically labeled complexes, $(CpR_n)_2Zr(CH_2CDMe_2)(D)$, in quantitative yield (^{1}H NMR). In benzene solution, $Cp^*_2Zr(CH_2CDMe_2)(D)$ undergoes isotopic rearrangement, affording both $Cp^*_2Zr(CHDCHMe_2)(D)$ and $Cp^*_2Zr\{CH_2CH(CH_2D)(CH_3)\}(D)$ (eq 3).[10] $(\eta^5\text{-}C_5Me_4H)_2Zr(CH_2CDMe_2)(D)$ exhibits similar


(3)

behavior. Moreover, addition of propylene to a benzene solution of pure $Cp^*_2Zr(CH_2CDMe_2)(D)$ or $(\eta^5\text{-}C_5Me_4H)_2Zr(CH_2CDMe_2)(D)$ results in rapid exchange between free olefin and coordinated alkyl.

By following the kinetics of these reactions using $\{^1H\}^2H$ NMR spectroscopy, we measured a rate constant of $1.0(4) \times 10^{-8}$ s^{-1} for the rearrangement of $Cp^*_2Zr(CH_2CDMe_2)(D)$ to $Cp^*_2Zr(CHDCHMe_2)(D)$ and $Cp^*_2Zr\{CH_2CH(CH_2D)(CH_3)\}(D)$ at 296 K in approximately equal amounts. No measurable deuterium isotope effect was observed. The corresponding rate constant for $(\eta^5\text{-}C_5Me_4H)_2Zr(CH_2CDMe_2)(D)$ is $4.3(4) \times 10^{-7}$ s^{-1} at 296 K. Several other zirconocene isobutyl deuteride complexes were examined (e.g., $Cp^*(\eta^5\text{-}C_5H_4CMe_3)Zr(CH_2CDMe_2)(D)$, $Cp^*CpZr(CH_2CDMe_2)(D)$), but reliable kinetic data could not be obtained.

Reaction of $(CpR_n)_2ZrH_2$ with 1 equiv of $^{13}CH_2{=}CHCH_3$ results in quantitative formation (^{1}H NMR) of $(CpR_n)_2Zr(^{13}CH_2CH_2CH_3)(H)$. Addition of excess propylene or other α-olefins results in reductive elimination of propane and formation of products derived from the resulting $[(CpR_n)_2Zr(II)]$.[11] Monitoring a benzene-d_6 solution of $Cp^*_2Zr(^{13}CH_2CH_2CH_3)(H)$ by ^{13}C NMR spectroscopy reveals isomerization, affording $Cp^*_2Zr(CH_2CH_2{}^{13}CH_3)(H)$ (eq 4) with $k^{296\ K} = 1.2 \times 10^{-4}$ s^{-1}. Similar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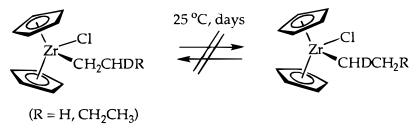
isomerizations are observed for $(\eta^5\text{-}C_5Me_4H)_2Zr(^{13}CH_2CH_2CH_3)(H)$ to $(\eta^5\text{-}C_5Me_4H)_2Zr(CH_2CH_2{}^{13}CH_3)(H)$ ($k^{296\ K} = 1.1 \times 10^{-3}$ s^{-1}) and for $Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)Zr(^{13}CH_2CH_2CH_3)(H)$ to $Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)Zr(CH_2CH_2{}^{13}CH_3)(H)$; the rate of the latter is too fast to measure using simple NMR spectral monitoring.

To determine the effect of the "spectator" ligand (hydride in the examples above) on the rate of alkyl isomerization, several alkyl complexes derived from Schwartz's reagent, $[Cp_2Zr(H)(Cl)]_n$[12] (**3**), were prepared. Although **3** is an insoluble polymeric material, its reaction with olefins affords soluble, well-characterized zirconocene alkyl chloride complexes, $Cp_2Zr(R)(Cl)$.[13] Thus, reaction of **3** with 1-butene, ethylene, propylene, and isobutylene affords $Cp_2Zr(CH_2CH_2CH_2CH_3)(Cl)$ (**4**), $Cp_2Zr(CH_2CH_3)(Cl)$ (**5**), $Cp_2Zr(CH_2CH_2CH_3)(Cl)$ (**6**), and $Cp_2Zr(CH_2CHMe_2)(Cl)$ (**7**). Benzene solutions of $Cp_2Zr(CH_2CHDCH_2CH_3)(Cl)$ and $Cp_2Zr(CH_2CH_2D)(Cl)$, prepared from $[Cp_2Zr(D)(Cl)]_n$ and the appropriate olefin, display a single peak in the $\{^1H\}^2H$ NMR spectrum. No change is observed over the course of 1 week at 296 K. Thus, there is no evidence for rearrangement of these terminal alkyls via β-H elimination under these conditions (eq 5). Likewise, a solution of $Cp_2Zr(^{13}CH_2CH_2CH_3)(Cl)$ does not undergo isotopic rearrangement at 296 K. Furthermore, addition of 5 equiv of $^{13}CH_2{=}CHCH_3$ to a solution of $Cp_2Zr(CH_2CH_2CH_3)(Cl)$ (**6**) in benzene-d_6 resulted in no incorporation of ^{13}C into the propyl group over the course of 1 week (eq 6).



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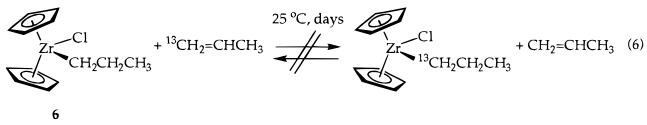

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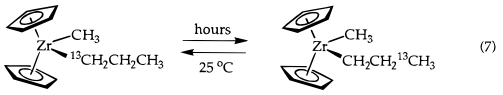
Reaction of $[Cp_2Zr(CH_3)(\mu_2\text{-}H)]_2$[14] with $^{13}CH_2{=}CHCH_3$ affords $Cp_2Zr(CH_3)(^{13}CH_2CH_2CH_3)$ in quantitative yield (^{1}H NMR). Over the course of 3 h at room temperature, $Cp_2Zr(CH_3)(^{13}CH_2CH_2CH_3)$ isomerizes to $Cp_2Zr(CH_3)(CH_2CH_2{}^{13}CH_3)$ (eq 7). Addition of $^{13}CH_2{=}CHCH_3$ to a benzene suspension of



(7)

$[Cp_2ZrH_2]_n$ results in formation of dimeric $[Cp_2Zr(^{13}CH_2CH_2CH_3)(\mu_2\text{-}H)]_2$, which undergoes isomerization to $[Cp_2Zr(CH_2CH_2{}^{13}CH_3)(\mu_2\text{-}H)]_2$ over 5 days at room temperature.

Hydrozirconation of Internal Olefins with $[Cp_2Zr(H)(Cl)]_n$. $Cp_2Zr(cyclo\text{-}C_5H_9)(Cl)$ (**8**) and $Cp_2Zr(cyclo\text{-}2\text{-}D\text{-}C_5H_8)(Cl)$ are obtained from addition of cyclopentene to a suspension of **3** or **3**-*d* in either benzene or diethyl ether. The unlabeled complex has been isolated as bright yellow crystals that are stable under vacuum. Cooling an Et_2O solution of **8** to −40 °C affords clear yellow crystals suitable for X-ray diffraction. As shown in Figure 1, the cyclopentyl ligand adopts an envelope conformation.

The $\{^1H\}^2H$ NMR spectrum of a benzene solution of $Cp_2Zr(cyclo\text{-}2\text{-}D\text{-}C_5H_8)(Cl)$ containing a 10-fold excess of cyclopentene initially exhibits only one resonance at $\delta = 1.43$ ppm, corresponding to deuterium at the 2-position of the cyclopentyl ligand. After 12 h at 296 K, a new peak appears at $\delta = 2.19$ ppm that has been identified as free cyclopentene-3-d_1. Over a

(10) Exchange between the hydride ligand and the coordinated alkyl group is also observed, producing complexes with two deuterium labels in the isobutyl group and hydrogen on zirconium.

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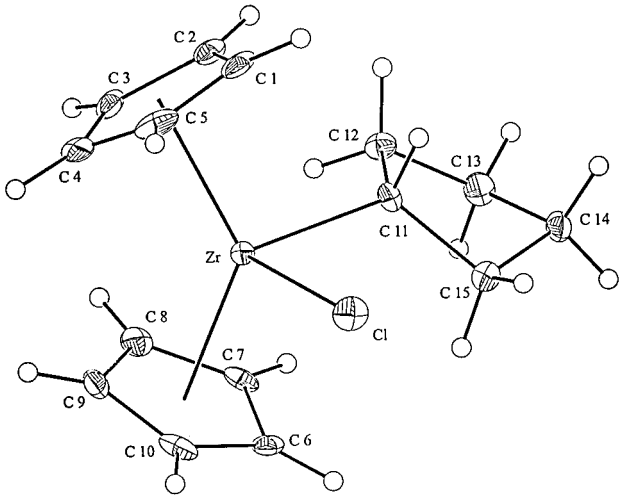


Figure 1. Molecular structure of $Cp_2Zr(cyclo\text{-}C_5H_9)(Cl)$ (**8**) (50% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å): Zr−Cent(1), 2.2305(7); Zr−Cent(2), 2.2094(7); Zr−C(11), 2.276(5); Zr−Cl, 2.4373(18). Bond angles (deg): Cent(1)−Zr−Cent(2), 130.83(3); C(11)−Zr−Cl, 93.85(13). Cent(1) is the centroid formed by C(1), C(2), C(3), C(4), and C(5). Cent(2) is the centroid formed by C(6), C(7), C(8), C(9), and C(10).

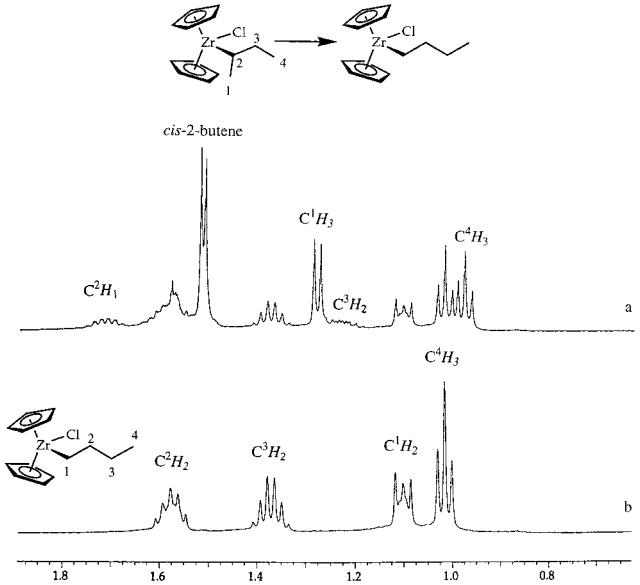
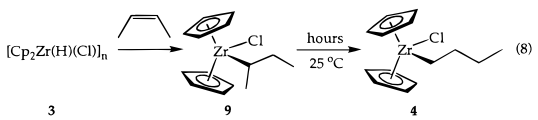


Figure 2. 500-MHz ^{1}H NMR spectra of the butyl resonances following hydrozirconation of *cis*-2-butene (a) after 6 h and (b) after 3 days.

period of 5 days, deuterium appears in the remaining positions of the Zr-bound cyclopentyl ring and the free cyclopentene.

Reaction of **3** with *cis*-2-butene has also been studied by ^{1}H NMR spectroscopy. After 35 min at room temperature, the NMR spectrum displays resonances attributable to $Cp_2Zr\{CH(CH_3)CH_2CH_3\}(Cl)$ (**9**), as shown in Figure 2. Over the course of hours at room temperature, the peaks for **9** are replaced by resonances for $Cp_2Zr(CH_2CH_2CH_2CH_3)(Cl)$ (**4**) (eq 8). Changing the solvent



from benzene to THF has no discernible effect on the rate of isomerization. During the isomerization of **9** to **4**, formation of *trans*-2-butene is observed by NMR. Furthermore, addition of

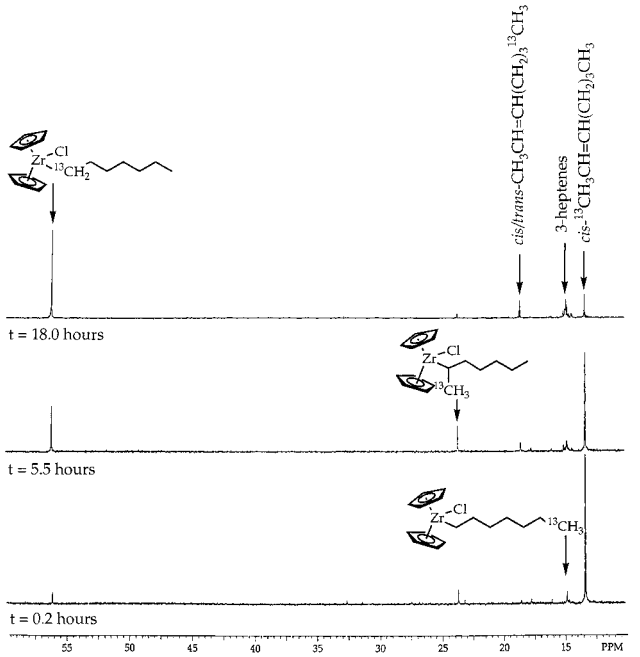
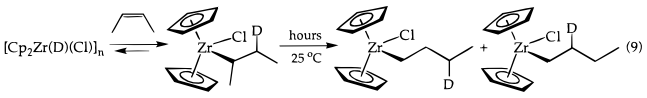


Figure 3. 125.77-MHz $\{^1H\}^{13}C$ NMR spectra of the heptyl resonances following hydrozirconation of *cis*-$^{13}CH_3CH{=}CHCH_2CH_2CH_2CH_3$. Conversion of $Cp_2Zr\{CH(^{13}CH_3)(CH_2)_4CH_3\}(Cl)$ to other isomers is observed, predominantly $Cp_2Zr\{^{13}CH_2(CH_2)_5CH_3\}(Cl)$ and C_7 of $Cp_2Zr\{CH_2(CH_2)_5{}^{13}CH_3\}(Cl)$.

1-pentene to a mixture containing only **9** and **4** results in buildup of $Cp_2Zr(CH_2CH_2CH_2CH_2CH_3)(Cl)$ (**10**) during the course of isomerization.

Twenty minutes after addition of **3**-*d* to *cis*-2-butene (benzene-d_6, 296 K), the $\{^1H\}^2H$ NMR spectrum displays a singlet at $\delta = 1.20$ ppm, assigned to the β-deuterium of $Cp_2Zr\{CH(CH_3)CHDCH_3\}(Cl)$. Over the course of several hours at this temperature, singlets at $\delta = 1.31$ and 1.47 ppm appear in an approximately 2:1 ratio, with gradual disappearance of the resonance at $\delta = 1.20$ ppm. No further change in the ^{1}H NMR spectrum is observed, even after weeks at room temperature. The peaks at δ 1.31 and 1.47 ppm are assigned to the deuterons at positions C_3 and C_2, respectively, of **4** (eq 9). No signal attributable to deuterium in the terminal positions (C_1 and C_4) of **4** is observed.



Reactions of $[Cp_2Zr(H)(Cl)]_n$ (**3**) with several longer chain olefins have also been examined. Monitoring the reaction of **3** with *cis*-2-hexene, *trans*-2-hexene, and *trans*-3-hexene by ^{1}H NMR indicates that internal alkyl complexes are likely present at early conversion times, but the identities and relative amounts of these species could not be definitively established due to the complexity of the ^{1}H NMR spectra. In the expectation that the ^{13}C NMR spectra would be much more readily interpretable, 1-^{13}C-*cis*-2-heptene, *cis*-$^{13}CH_3CH{=}CHCH_2CH_2CH_2CH_3$, was prepared by addition of $^{13}CH_3I$ to $LiC{\equiv}CCH_2CH_2CH_2CH_3$ in liquid ammonia, followed by hydrozirconation of the alkyne and quenching with H_2O.

The ^{13}C NMR spectrum (Figure 3) for the reaction of **3** with ca. 1.3 equiv of *cis*-$^{13}CH_3CH{=}CHCH_2CH_2CH_2CH_3$ in benzene-d_6 after 10 min at 296 K exhibits a resonance at $\delta = 23.45$ ppm attributable to $Cp_2Zr\{CH(^{13}CH_3)(CH_2)_4CH_3\}(Cl)$ and additional resonances at $\delta = 56.0$ and 14.7 ppm, assigned to C_1

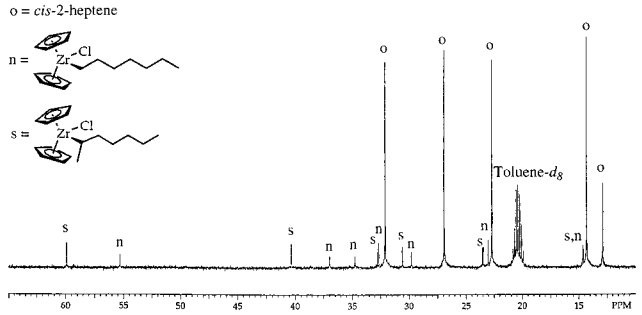
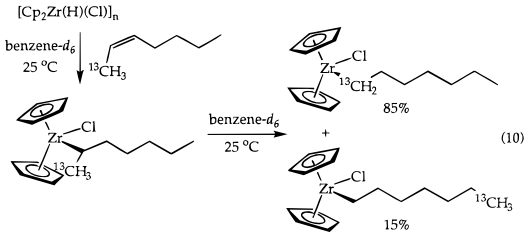
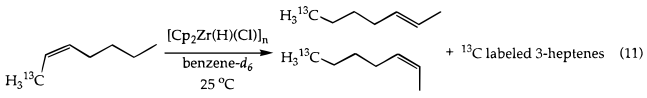


Figure 4. Upfield region of the 125.77-MHz $\{^1H\}^{13}C$ NMR spectrum obtained at 240 K, following the hydrozirconation of *cis*-2-heptene with **3**.

of $Cp_2Zr\{^{13}CH_2(CH_2)_5CH_3\}(Cl)$ and C_7 of $Cp_2Zr\{CH_2(CH_2)_5{}^{13}CH_3\}(Cl)$, respectively. The resonance due to $Cp_2Zr\{CH(^{13}CH_3)(CH_2)_4CH_3\}(Cl)$ grows to a maximum relative intensity of ca. 50% over a period of about 5 h and then decreases as those attributable to $Cp_2Zr\{^{13}CH_2(CH_2)_5CH_3\}(Cl)$ and C_7 of $Cp_2Zr\{CH_2(CH_2)_5{}^{13}CH_3\}(Cl)$ continue to grow until, after about 48 h, they are the only resonances attributable to an organometallic compound. During this period, their ratio remains constant at 85:15 (eq 10).[15] For confirmation of these assignments, the hydrozirconation of unlabeled *cis*-2-heptene was carried out in toluene-d_8 for 3 h at 296 K, and the reaction was then cooled to −50 °C to prevent further isomerization. The ^{13}C NMR spectrum of the reaction mixture was recorded at this temperature (Figure 4). Evident are 14 resonances that correspond to heptyl resonances of two organozirconium complexes, assigned as $Cp_2Zr\{CH_2(CH_2)_5CH_3\}(Cl)$ and $Cp_2Zr\{CH(CH_3)(CH_2)_4CH_3\}(Cl)$. Perhaps the most informative feature of the spectrum is the region between $\delta = 50$ and 60 ppm, where carbons directly bound to zirconium generally resonate. In this region, only two peaks are observed, one at $\delta = 56.0$ ppm assigned to C_1 of $Cp_2Zr\{CH_2(CH_2)_5CH_3\}(Cl)$ and the other at $\delta = 59.8$ ppm assigned to the methine carbon of $Cp_2Zr\{CH(CH_3)(CH_2)_4CH_3\}(Cl)$.



In addition to peaks corresponding to $Cp_2Zr\{^{13}CH_2(CH_2)_5CH_3\}(Cl)$, $Cp_2Zr\{CH_2(CH_2)_5{}^{13}CH_3\}(Cl)$, and $Cp_2Zr\{CH(^{13}CH_3)(CH_2)_4CH_3\}(Cl)$, the ^{13}C NMR spectrum shown in Figure 3 exhibits resonances assigned to terminally ^{13}C-labeled isomeric 2-heptenes, based on comparison to authentic samples, along with smaller signals believed to be due to ^{13}C-labeled isomeric 3-heptenes (eq 11). The largest peak at $\delta = 18.3$ ppm corresponds to both 7-^{13}C-*cis*-2-heptene and 7-^{13}C-*trans*-2-heptene.



(15) A small amount of $Cp_2Zr\{CH(CH_3)(CH_2)_4{}^{13}CH_3\}(Cl)$ may be formed during the isomerization reaction, but we were unable to detect such a species due to overlapping ^{13}C NMR resonances (see Figure 4).

Table 1. Deuterium Labeling of Butanes Obtained by Hydrozirconation of *cis*-2-Butene, Followed by CH_3OD Quench at Various Times

time (h)	% butane-2-d_1	% butane-1-d_1
0.3	100	0
6.0	55	45
13.0	38	62
25.0	20	80
35.0	14	86
47.8	8	92
61.0	0	100
1.0[a]	20	80

[a] Hydrozirconation of *cis*-2-butene in the presence of excess **3**.

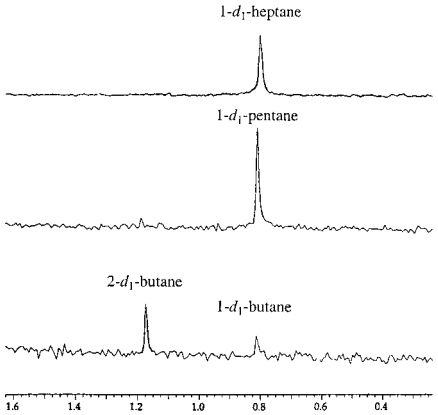
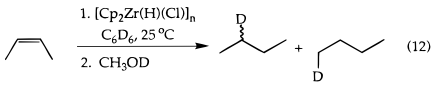


Figure 5. 76.77-MHz $\{^1H\}^2H$ NMR spectra of the deuterated alkanes produced by treatment of $[Cp_2Zr(H)(Cl)]_n$ (**3**) with *cis*-2-butene, *cis*-2-pentene, and *cis*-2-heptene, followed by a CH_3OD quench.

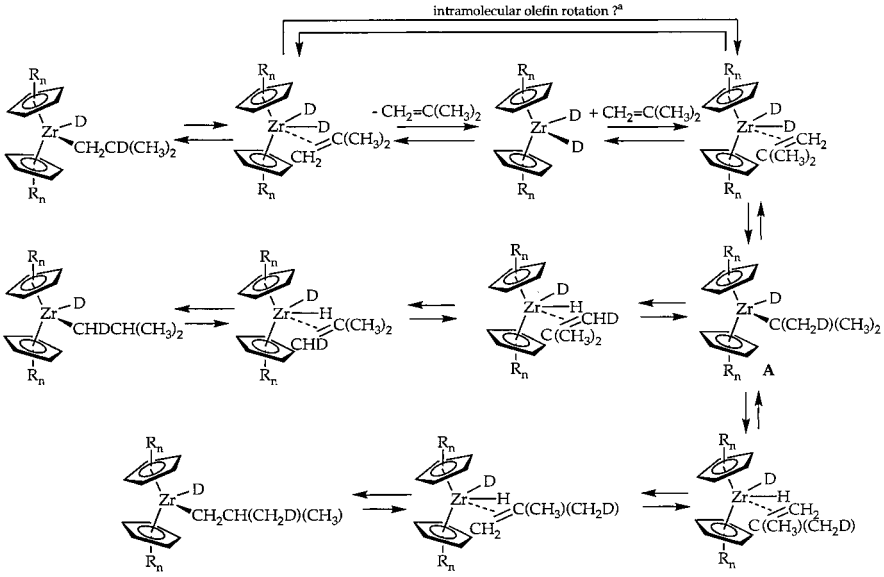
The course of hydrozirconation of *cis*-2-butene in benzene solution was also followed by quenching with CH_3OD at various time intervals (eq 12); results are given in Table 1. $\{^1H\}^2H$ NMR



spectroscopy reveals that, at short reaction times (up to about 20 min), only 2-deuteriobutane is formed, whereas with longer reaction times increasing amounts of 1-deuteriobutane are obtained. The time variation of the ratio of 1- and 2-deuterated butanes is consistent with the rate of isomerization of $Cp_2Zr\{CH(CH_3)CH_2CH_3\}(Cl)$ to $Cp_2Zr(CH_2CH_2CH_2CH_3)(Cl)$, as monitored directly by ^1H NMR (vide supra).

For the hydrozirconation of longer internal olefins such as *cis*-2-pentene and *cis*-2-heptene in benzene solution, quenching after 1 h with CH_3OD results in solely *terminally* deuterated alkane. The $^2H\{^1H\}$ NMR spectra of the deuterated alkanes obtained after 1 h of hydrozirconation are shown in Figure 5. These results suggest that rearrangements of the internal to the primary alkyls are relatively rapid, in contrast to the conclusions obtained by directly monitoring the reaction of **3** with *cis*-$^{13}CH_3CH{=}CHCH_2CH_2CH_2CH_3$ by ^{13}C NMR spectroscopy. In an attempt to reconcile this discrepancy, 10 mol % of CH_3OD was added after the hydrozirconation of *cis*-2-heptene had proceeded 1 h, and the reaction was monitored by low-temperature ^{13}C NMR spectroscopy; $Cp_2Zr\{CH_2(CH_2)_5CH_3\}(Cl)$ is the only (remaining) heptylzirconium product observed. However, when an identical experiment is performed with *cis*-2-butene, both internal and terminal organozirconium products are observed in the ^{13}C NMR spectrum, also in agreement with the corresponding quenching experiment. Since after 1 h the hydrozirconation of *cis*-2-heptene with (insoluble) **3** results in relatively

Scheme 1



[a] Uncertainty concerning olefin dissociation/reassociation vs intramolecular rotation applies to all olefin hydride intermediates.

low conversion of the olefin to the zirconium alkyl as compared to the hydrozirconation of *cis*-2-butene, we examined the effect of removing unreacted **3** from the reaction mixture before the addition of methanol. Removal of unreacted **3** can be accomplished by filtration, resulting in a clear yellow solution. Addition of CH_3OD to the filtrate, followed by analysis by $\{^1H\}^2H$ NMR, reveals that both internally and terminally deuterated heptanes are produced. To further demonstrate the effects of unreacted **3** on the quenching of hydrozirconation reactions, we added *cis*-2-butene to a 2-fold excess of **3**, followed by quenching with CH_3OD after 1 h. This procedure results in a substantial increase in the amount of terminally deuterated butane as compared to the stoichiometric reaction.

Discussion

Rearrangements of Isotopically Labeled $(CpR_n)_2Zr(CH_2CHR'_2)(H)$. Complexes of the general formula $(CpR_n)_2Zr(CH_2CHR_2')(H)$ (R, R′, R″ = alkyl, H) are readily prepared from $(CpR_n)_2ZrH_2$ and the appropriate olefin, $CH_2{=}CR'R''$. We have previously shown that, although these complexes are stable in solution at 296 K, they undergo facile, reversible β-H elimination. Using methyl-*tert*-butylacetylene to rapidly trap $(CpR_n)_2ZrH_2$, similar to a procedure used earlier,[16] rate constants for β-H elimination have been measured for the $(CpR_n)_2Zr(CH_2CHR_2')(H)$ (CpR_n = (η^5-C_5Me_5) (Cp*), (η^5-C_5Me_4H)) systems examined here, as well as for several other substituted zirconocenes.[9] Isotopically labeled alkyl complexes undergo rearrangement under the same conditions, but the rates of rearrangement are generally 10^2-10^4 times slower than the rates of β-H elimination.

A proposed mechanism for deuterium migration in $(CpR_n)_2Zr(CH_2CDMe_2)D$ is shown in Scheme 1; similar paths can account for all the isotopic rearrangements observed. Following β-H elimination and olefin reorientation, either through intramolecular olefin rotation or by dissociation and recoordination in the opposite direction, β-H migratory insertion affords secondary or tertiary alkyl hydride species. Since all alkyl hydride complexes studied undergo very rapid exchange with free olefin, we favor the olefin dissociation pathway, although the presence of an olefin dihydride intermediate which undergoes olefin rotation faster than dissociation cannot be ruled out definitively. The secondary or tertiary alkyl hydride intermediate then undergoes β-H elimination and readdition to form the primary alkyl with the label in a new position.

A mechanism similar to that shown in Scheme 1 has been proposed by Busico et al. to account for the tacticity dependence on monomer concentration in metallocene-catalyzed olefin polymerization, where lower propylene pressures result in decreased stereospecificity.[6c] At low propylene concentrations, epimerization at the methine carbon of the last inserted monomer unit competes with olefin insertion, hence decreasing the isotacticity of the resulting polypropylene. A sequence of β-H elimination and reinsertion steps leads to formation of the tertiary alkyl intermediate [Zr-C(CH$_3$)$_2$**P**] (**P** = polymer chain), which may β-H eliminate from either methyl group to re-form the original [ZrCH$_2$CH(CH$_3$)**P**] or the enantiomeric equivalent. Busico favors the olefin rotation pathway over the free olefin route, since it is commonly accepted that α-olefins undergo insertion at a much greater rate than the corresponding *gem*-disubstituted olefins.[6]

The rate of alkyl isomerization is influenced by the degree of substitution on the cyclopentadienyl ligands: more substituted cyclopentadienyl ligands slow the rate of the reaction.[9] For the ^{13}C-labeled propyl hydride complexes, the relative rate of isotopic rearrangement is [Cp*(η^5-C_5H_4−CMe_3)Zr] > [(η^5-C_5Me_4H)$_2$Zr] > [Cp*$_2$Zr]. Similarly, the rate of deuterium scrambling in the labeled isobutyl deuteride complexes is [(η^5-C_5Me_4H)$_2$Zr] > [Cp*$_2$Zr]. In both cases, the effect of changing the cyclopentadienyl substitution has a relatively modest effect on the rate of isotopic rearrangement. For example, the rate enhancement from removing two methyl groups results in a 40-fold increase in the rate constant at 296 K.

Since the rates for olefin insertion and β-H elimination are more than 2 orders of magnitude faster than the rates of isotopic rearrangement, we conclude that the formation of the more substituted alkyl complex (either secondary or tertiary) is the rate-determining step in the isomerization process of Scheme 1. This assertion is supported by the failure to observe any intermediate internal alkyl complex in these systems. We have observed similar behavior for the addition of *cis*-2-butene to

(16) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

$Cp^*_2ZrH_2$, where the addition of the zirconium hydride bond is much slower than isomerization of the internal alkyl to the final, only observable, terminal product, $Cp^*_2Zr(CH_2CH_2CH_2CH_3)(H)$.[9]

The rate constant at 296 K for β-H elimination[17] of the isobutyl ligand from $Cp^*_2Zr(CH_2CHMe_2)(H)$ is much greater than the rate constant for the isomerization ($k_{\beta-H} = 2.8 \times 10^{-6}$ s^{-1}; $k_{isom} = 1.0 \times 10^{-8}$ s^{-1}; $k_{\beta-H}/k_{isom} = 280$) for $Cp^*_2Zr(CH_2CDCMe_2)(D)$ to $Cp^*_2Zr(CHDCHMe_2)(D)$ and $Cp^*_2Zr(CH_2CH(CH_2D)(CH_3))(D)$.[9] By comparison, for the related propyl hydride complex $Cp^*_2Zr(^{13}CH_2CH_2CH_3)(H)$, these rates are much greater and the ratio of rates smaller ($k_{\beta-H} = 1.1 \times 10^{-3}$ s^{-1}; $k_{isom} = 1.2 \times 10^{-4}$ s^{-1}; $k_{\beta-H}/k_{isom} = 11$).[9] These data indicate that the isopropyl hydride intermediate is more accessible than the *tert*-butyl hydride intermediate implied in the rearrangement shown in eq 3 (**A** in Scheme 1). Apparently, the presence of an additional methyl group in the case of the *tert*-butyl intermediate sterically disfavors its formation relative to the isopropyl complex, which then in turn decreases the rates of isomerization (as well as β-H elimination).

Rearrangements of $Cp_2Zr(CH_2CHR'_2)(X)$ ($R' = H$, Me, Et; $X = H$, Me, Cl). Changing the "spectator" ligand in the metallocene wedge from hydride to other one-electron ("X-type") ligands has a relatively larger effect on the rates of β-H elimination and alkyl isomerization. Whereas $Cp^*(C_5H_4CMe_3)Zr(CH_2CHR'_2)(H)$ ($R' = H$, Me, Et) compounds undergo facile β-H elimination at 296 K, the corresponding compounds $Cp_2Zr(CH_2CHR'_2)(Cl)$ ($R' = H$, Me, Et) are stable to β-H elimination/olefin rotation/reinsertion, as demonstrated by the lack of deuterium scrambling and the lack of isotopic rearrangement for $Cp_2Zr(^{13}CH_2CH_2CH_3)(Cl)$. The observation that $Cp_2Zr(CH_2CH_2CH_3)(Cl)$ does not exchange with $^{13}CH_2{=}CHCH_3$ also is in agreement with the very inert nature of these alkyl/chloro complexes. A general lack of β-H elimination from primary alkyl complexes of the type $Cp_2Zr(CH_2CHR'_2)(Cl)$ was originally proposed by Schwartz,[18] based on the absence of alkyl exchange with olefins in the related cyclohexylmethyl complex, $Cp_2Zr(CH_2\text{-}cyclo\text{-}C_6H_{11})(Cl)$.

To establish whether this effect is steric or electronic in origin, the labeled propyl methyl complex $Cp_2Zr(^{13}CH_2CH_2CH_3)(CH_3)$ was prepared.[19] Isotopic rearrangement is observed over the course of 3 h at 296 K. Since methyl and chloride are approximately isosteric, the difference in reactivity must, therefore, be due to electronic properties, most likely the π-donating ability of the chloride ligand. Lone electron pair donation from Cl into the $1a_1$ zirconocene orbital formally completes the 18-electron zirconocene valence shell, and hence, unlike $Cp_2Zr(CH_2CHR'_2)(X)$ ($X = H$, CH_3), there is no empty (strictly) nonbonding orbital for β-H elimination.[20] Alkyl isomerization initiated by β-H elimination should be very facile for zirconocene cations, $[Cp_2Zr(CH_2CHR'_2)]^+$, since formally there are two empty nonbonding orbitals.[21]

We considered the possibility that small, undetectable amounts of the dihydride complex, $[Cp_2ZrH_2]_n$, might promote propyl isomerization for $Cp_2Zr(^{13}CH_2CH_2CH_3)(CH_3)$, since preparation of $[Cp_2Zr(CH_3)(H)]_2$ involves hydrogenation of Cp_2ZrMe_2. $[Cp_2Zr(^{13}CH_2CH_2CH_3)(H)]_2$ was therefore prepared via treatment of $[Cp_2ZrH_2]_n$ with $^{13}CH_2{=}CHCH_3$. Isotopic rearrangement for $[Cp_2Zr(^{13}CH_2CH_2CH_3)(H)]_2$ does occur over the course of 5 days at 296 K but at a rate much slower than that observed for $Cp_2Zr(^{13}CH_2CH_2CH_3)(CH_3)$. The slow isomerization rate for $[Cp_2Zr(^{13}CH_2CH_2CH_3)(H)]_2$ is attributed to its dimeric nature in solution. Schwartz has previously reported the robust nature of these alkyl hydride complexes, a result of their strong bridging hydride interactions.[18] Presumably, the dimeric alkyl hydride must dissociate into the 16-electron monomeric species in order to undergo β-H elimination, eventually resulting in isotopic scrambling.

Hydrozirconation of Internal Olefins and Isomerization of Internal Alkyls. In contrast to primary alkyl complexes of $Cp_2Zr(R)(Cl)$, internal acyclic and cyclic alkyl complexes readily undergo β-H elimination and alkyl isomerization reactions. The formation of terminal products from hydrozirconation of internal olefins was a striking observation in early studies.[3,4] It is this behavior that has made hydrozirconation a valuable synthetic tool for a variety of transformations.[4] The order of reactivity based on qualitative observations is terminal alkene > internal alkene > exocyclic alkene > cyclic alkene $\approx$ trisubstituted alkene.[4c] For example, only the zirconium-2-cyclohexenylethyl complex is observed upon the hydrozirconation of vinylcyclohexene.[22] Isomerization of the internal alkyl adduct has been generally believed to be much faster than its initial formation by reaction of internal olefin with polymeric **3**, since no internally substituted products are isolated from treatment of the organozirconium complex with various electrophiles. For example, the hydrozirconation of (*Z*)-5-decene at 40 °C for 4 h, followed by addition of D_2O, resulted in formation of up to 70% decane-1-d_1, with the remaining products identified as internal decenes; no internally deuterated decanes were detected.[23] Tertiary alkylzirconium complexes, e.g., $Cp_2Zr(CMe_3)(Cl)$, appear to be generally inaccessible even as intermediates. Attempted hydrozirconation of an internal alkene which is capped at both ends with *tert*-butyl groups yields only isomerized alkene.[23]

Direct analysis of the hydrozirconation of *cis*-2-butene by high-field ^1H NMR spectroscopy has now provided the first observation of a transient zirconium internal alkyl complex, $Cp_2Zr\{CH(CH_3)CH_2CH_3\}(Cl)$ (**9**).[24] The isomerization of **9** to $Cp_2Zr(CH_2CH_2CH_2CH_3)(Cl)$ (**4**) occurs over the course of several hours at 296 K, which is slower than the time required for the complete reaction of $[Cp_2Zr(H)(Cl)]_n$ (**3**). Clearly, the rate of alkyl isomerization in the butyl case is not as rapid as previously believed.

The hydrozirconation of *cis*-2-butene with **3**-*d* also confirms the formation of **9**. The $^2H\{^1H\}$ NMR spectrum initially displays one peak, attributable to the β-deuterium of $Cp_2Zr\{CH(CH_3)CHDCH_3\}(Cl)$.[25] The proposed mechanism for isomerization

(17) Rates were measured by trapping the intermediate zirconium dihydride with dialkylacetylene trapping, as described previously: Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566−1577. With only moderate amounts of acetylene, the observed rates were found to be independent of acetylene concentration. See Experimental Section for details.

(18) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1840.

(19) This complex slowly decomposes in solution over the course of several days at room temperature. Access to Zr(II)-derived compounds from dialkyl zirconocenes has been noted previously. See, for example: Negishi, E. I.; Montchamp, J.-L. in *Metallocenes, Vol. 1*; Togni, A., Halterman, R. L., Eds.; VCH: Weinheim, 1998; Chapter 5.

(20) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(21) Current studies are underway to measure the rates of isomerization in related alkyl zirconocene cations. Wendt, O. F.; Bercaw, J. E., unpublished results.

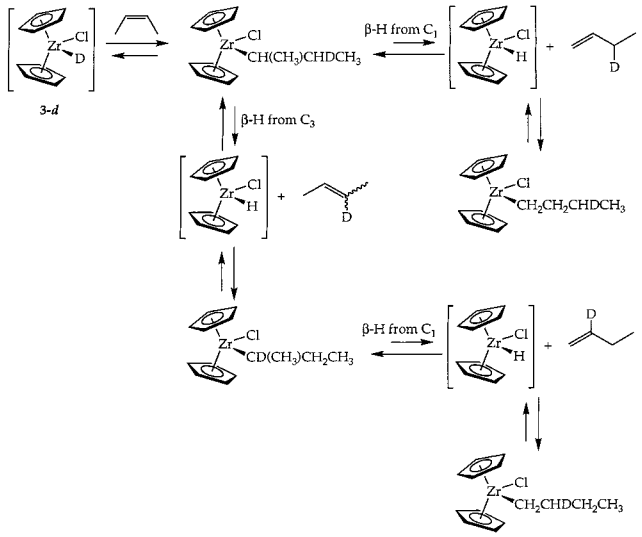
(22) Negishi, E.; Miller, J. A.; Yoshida, T. *Tetrahedron Lett.* **1984**, *25*, 3407.

(23) Annby, U.; Alvhäll, J.; Gronowitz, S.; Hallberg, A. *J. Organomet. Chem.* **1989**, *377*, 75.

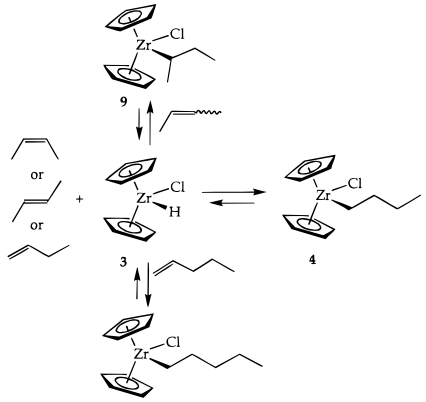
(24) Secondary alkyls have been observed for styrene and other related aryl substrates: see ref 13a.

(25) Relative rates of isomerization suggest that a detectable amount of **9**-2*d* should form during isomerization to **4**-2*d*. To date, we have been unable to detect such an intermediate by $^2H\{^1H\}$ NMR.

Scheme 2



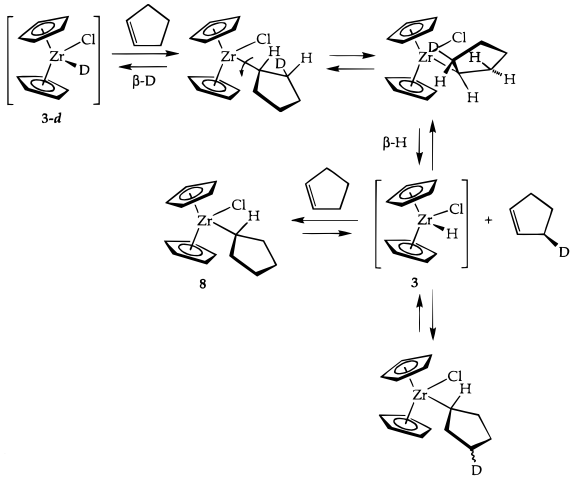
Scheme 3



of $Cp_2Zr\{CH(CH_3)CHDCH_3\}(Cl)$ to $Cp_2Zr(CH_2CH_2CHDCH_3)(Cl)$ and $Cp_2Zr(CH_2CHDCH_2CH_3)(Cl)$ is shown in Scheme 2. After addition of the olefin, the internal alkyl complex can β-H eliminate from either C_1 or C_3. If β-H elimination occurs from C_1, $[Cp_2Zr(H)(Cl)]$ and 1-butene-3-d_1 are formed, which then undergo insertion to form $Cp_2Zr(CH_2CH_2CHDCH_3)(Cl)$. If β-H elimination occurs from C_3, liberation of *cis*- or *trans*-2-butene-2-d_1 occurs with formation of $[Cp_2Zr(H)(Cl)]$. The 2-butenes then reinsert, forming another internal alkyl complex, now with deuterium on the carbon bound directly to zirconium. This then undergoes β-H elimination from C_1 to generate 1-butene-2-d_1, which then inserts, forming $Cp_2Zr(CH_2CHDCH_2CH_3)(Cl)$. The ratio of $Cp_2Zr(CH_2CH_2CHDCH_3)(Cl)$ to $Cp_2Zr(CH_2CHDCH_2CH_3)(Cl)$ is approximately 2:1 during the isomerization reaction, indicating that β-H elimination from C_1 is favored over elimination from C_3. No deuteration in the α or ω positions of **4** is observed, consistent with the inert nature of primary alkyls, since those isotopomers are accessed only by further rearrangement of $Cp_2Zr(CH_2CH_2CHDCH_3)(Cl)$ or $Cp_2Zr(CH_2CHDCH_2CH_3)(Cl)$.

The detection of *trans*-2-butene during isomerization of **9** to **4** suggests the intermediacy of $[Cp_2Zr(H)(Cl)]$ and free olefin, rather than olefin−hydride intermediates that undergo intramolecular olefin rotation. This conclusion is further supported by the addition of 1-pentene to a mixture of **9** and **4**. By the time **9** is completely gone, the pentyl chloride complex, $Cp_2Zr(CH_2CH_2CH_2CH_2CH_3)(Cl)$, is observed along with **4** (Scheme 3). Facile olefin exchange is not surprising for a d^0 metal complex that is not capable of stabilizing π-back-donation.

Scheme 4



The isomerization of the deuterium-labeled cyclopentyl chloride complex $Cp_2Zr(cyclo\text{-}2\text{-}D\text{-}C_5H_8)(Cl)$ also supports a free olefin pathway in alkyl isomerization. The fact that deuterium appears in free cyclopentene (cyclopentene-3-d_1) *before* it appears in positions other than the 2 position of **8** demonstrates that β-H elimination and liberation of free cyclopentene is the favored pathway over intramolecular olefin rotation and reinsertion (Scheme 4). Note that the absence of cyclopentene-1-d_1 is consistent with Scheme 4, since both the addition and elimination of Zr−H follow strict *syn* stereochemistry.

Alkyl length clearly has a significant effect on the rate of isomerization of internal alkyls. Hydrozirconation of *cis*-$^{13}CH_3CH{=}CHCH_2CH_2CH_2CH_3$ demonstrates that alkyl isomerization of the internal heptyl chloride complex is faster than that of the corresponding butyl complex, since $Cp_2Zr\{CH(^{13}CH_3)(CH_2)_4CH_3\}(Cl)$ disappears in less than 24 h, whereas **9** persists for several days. Isomerization of $Cp_2Zr\{CH(^{13}CH_3)(CH_2)_4CH_3\}(Cl)$ produces both $Cp_2Zr\{^{13}CH_2(CH_2)_5CH_3\}(Cl)$ and $Cp_2Zr\{CH_2(CH_2)_5{}^{13}CH_3\}(Cl)$, consistent with isomerization in both directions down the alkyl chain, while ^{13}C NMR spectroscopy reveals that only one internal alkyl complex, $Cp_2Zr\{CH(^{13}CH_3)(CH_2)_4CH_3\}(Cl)$, is formed in appreciable concentration. Formation of $Cp_2Zr\{CH_2(CH_2)_5{}^{13}CH_3\}(Cl)$ implies the intermediacy of 3- and 4-heptyl zirconium complexes, although we have been unable to detect these complexes spectroscopically. Based on this evidence, we propose that the rate of isomerization for 3- and 4-heptyl complexes is rapid, such that only the 2-isomer can be observed. Unfavorable steric interactions between alkyl chains longer than methyl and the chloride ligand in the 3- and 4-heptyl zirconocene presumably result in destabilization and hence faster rates of isomerization. Although reliable force fields are not available, molecular mechanics[26] calculations support this assertion. Of the internal alkyl complexes, $Cp_2Zr\{CH(CH_3)(CH_2)_4CH_3\}(Cl)$ was found to be approximately 2 kcal·mol^{-1} more stable than $Cp_2Zr\{CH(CH_2CH_2CH_2CH_3)(CH_2CH_3)\}(Cl)$, which in turn is about 3 kcal·mol^{-1} more stable than $Cp_2Zr\{CH(CH_2CH_2CH_3)_2\}(Cl)$.

In addition to directly observing internal alkyl complexes by NMR spectroscopy, we have looked for these species in quenching reactions. Hydrozirconation of *cis*-2-butene followed by addition of CH_3OD affords mixtures of internally and terminally deuterated alkanes. For hydrozirconation in the

(26) Molecular mechanics calcuations (MM2 level) were performed using CAChe molecular modeling software using the structural parameters obtained from the solid-state structure of **11**.

presence of excess *cis*-2-butene, internally deuterated butanes are observed for up to 48 h, much longer than previously reported.[4c] The ratio of internally to terminally deuterated butanes obtained from the quenching experiments corresponds roughly to the amounts of internal and terminal butyl organozirconium complexes that were detected by direct NMR observation.

By contrast, addition of CH_3OD to reaction mixtures of $[Cp_2Zr(H)(Cl)]_n$ with *cis*-2-pentene or *cis*-2-heptene results in *only* terminally deuterated alkanes. These results appear inconsistent with those obtained by monitoring the reaction by NMR spectroscopy. To resolve the discrepancy, we first examined the solution obtained from hydrozirconation of *cis*-2-heptene for 1 h, followed by addition of 10 mol % of CH_3OD by ^{13}C NMR. Only terminal zirconium heptyl complex was detected, suggesting methanol somehow catalyzes the isomerization of $Cp_2Zr\{CH(CH_3)(CH_2)_4CH_3\}(Cl)$ to $Cp_2Zr\{CH_2(CH_2)_5CH_3\}(Cl)$. By comparison, after hydrozirconation of *cis*-2-butene followed by addition of 10 mol % of methanol, both **9** and **4** are observed by low-temperature ^{13}C NMR spectroscopy, so methanol does not promote isomerization in this case.

Why might $Cp_2Zr\{CH(CH_3)CH_2CH_3\}(Cl)$ and $Cp_2Zr\{CH(CH_3)(CH_2)_4CH_3\}(Cl)$ behave differently? Qualitative comparison of the relative rates of hydrozirconation reveals that *cis*-2-butene reacts more rapidly than *cis*-2-heptene with $[Cp_2Zr(H)(Cl)]_n$ (**3**). This is in accord with previous observations that longer olefins undergo hydrozirconation at a slower rate than their less sterically crowded counterparts.[4c] Thus, after 1 h there is considerably more unreacted $[Cp_2Zr(H)(Cl)]_n$ during the hydrozirconation of *cis*-2-heptene than for *cis*-2-butene. We therefore postulated that methanol might react with the residual **3**, forming a small amount of an organozirconium species that catalyzes the isomerization of internal alkyl to terminal complex.

To test this hypothesis, we carried out the hydrozirconation of *cis*-2-heptene for 1 h, followed by removal of unreacted **3** by filtration and addition of CH_3OD to the clear yellow filtrate. In this case, $\{^1H\}^2H$ NMR spectroscopy showed formation of *both* internally and terminally deuterated heptanes (ca. 40:60, respectively). In the complementary experiment, hydrozirconation of *cis*-2-butene in the presence of *excess* **3** followed by quenching with CH_3OD results in enrichment of butane-1-d_1 (Table 1), presumably due to an increased concentration of the (as yet unidentified) isomerization catalyst.

While these results seem to contradict previous observations that the hydrozirconation of internal olefins yields only terminally substituted products, they are, in fact, not inconsistent. Typically, hydrozirconation reactions are performed using elevated temperatures and/or until a homogeneous solution is obtained, thus allowing isomerization of all internal alkyl adducts to the more stable terminal organozirconium complex. However, the isomerization of the internal alkyl adduct is not as rapid as previously reported, and internally functionalized alkanes *can* be prepared under the appropriate conditions. Furthermore, our results demonstrate that addition of electrophiles such as H^+ in the presence of unreacted **3** can promote alkyl isomerization. These results, in concert with normal practice, offer an explanation for the prior failure to observe any internal alkyl adducts.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere as described previously.[27] Argon, dinitrogen, dihydrogen, and dideuterium gases were purified by passage over columns of MnO on vermiculite and activated molecular sieves. Solvents for air- and moisture-sensitive reactions were stored under vacuum over titanocene.[28] Preparations of $Cp^*_2ZrH_2$,[29] $[Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrH_2]_2$,[8] $(\eta^5\text{-}C_5Me_4H)_2ZrH_2$,[8] $[Cp_2Zr(CH_3)(H)]_2$,[14] $[Cp_2Zr(Cl)(H)]_n$,[12] $[Cp_2Zr(Cl)(D)]_n$,[12] and $[Cp_2ZrH_2]_n$[18] were carried out as described previously.

NMR solvents were obtained and prepared as follows. Benzene-d_6, toluene-d_8, and tetrahydrofuran-d_8 were purchased from Cambridge Isotope Laboratories. Benzene-d_6 and toluene-d_8 were dried over $LiAlH_4$ and sodium and then stored over titanocene. Tetrahydrofuran-d_8 was dried over CaH_2 and stored over sodium/benzophenone ketyl. $^{13}CH_2{=}CHCH_3$ was purchased from Cambridge Isotope Laboratories and distilled on the vacuum line before use. $^{13}CH_3I$ and CH_3OD were purchased from Cambridge Isotope Laboratories and used as received. Ethylene was purchased from Matheson and passed through a trap maintained at −78 °C before use. Isobutene, *cis*-2-butene, and propene were purchased from Aldrich, dried over $Al(CH_2CHMe_2)_3$, and stored over 4-Å molecular sieves. 1-Pentene, 1-hexene, *cis*- and *trans*-2-hexene, *trans*-3-hexene, and cyclopentene were purchased from Aldrich, distilled from $LiAlH_4$, and stored over CaH_2. 2-Pentyne was purchased from Lancaster and used as received.

NMR spectra were recorded on a Bruker AM500 (500.13 MHz for ^1H, 76.77 for ^2H, 125.77 MHz for ^{13}C) spectrometer. All chemical shifts are relative to TMS using ^1H (residual), ^2H, or ^{13}C chemical shifts of the solvent as a secondary standard. For ^{13}C NMR experiments, 10 s relaxation delays were used to obtain reliable integration data. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey. Many of the alkyl complexes reported either decompose or form oils upon attempted isolation, therefore precluding elemental analysis.

$Cp^*_2Zr(CH_2CDMe_2)(D)$ (1). This compound was prepared in a manner similar to that reported previously.[11] In the drybox, a J. Young NMR tube was charged with 0.50 mL of a 0.0488 M stock solution (0.0244 mmol) of $Cp^*_2ZrH_2$ and 0.094 M Cp_2Fe in benzene-d_6. On the vacuum line, the solution was frozen and degassed with three freeze−pump−thaw cycles. The tube was then fully submerged in liquid nitrogen, and 1 atm of D_2 was admitted. The tube was thawed, shaken, and rotated at room temperature for 5 min, after which time the solution was again frozen and the tube evacuated. Via a 6.9-mL calibrated gas volume, 76 Torr (0.028 mmol) of isobutene was added at −196 °C. The tube was then thawed and shaken and monitored by ^1H NMR spectroscopy. Attempts to isolate solid samples produced an oil unsuited to elemental analysis. ^1H NMR (benzene-d_6): $\delta = 1.93$ (s, 30 H, Cp*), −0.049 (s, 2H, CH_2CDMe_2), 1.02 (s, 6H, CH_2CDMe_2). ^2H NMR (benzene): $\delta = 6.36$ (s, 1D, Zr-*D*), 1.91 (s, 1D, CH_2CDMe_2).

Isomerization of 1 and 2 As Monitored by $\{^1H\}^2H$ NMR. In the drybox, a flame-sealable NMR tube was charged with 0.50 mL of a 0.166 M stock solution of **1** or **2** containing 10 μL of benzene-d_6 in C_6H_6. On the vacuum line, the solution was frozen and degassed with three freeze−pump−thaw cycles. The entire tube was then immersed in liquid nitrogen, and 1 atm of D_2 was admitted. The tube was thawed and rotated. After 5 min, the tube was again frozen, and isobutene (230 Torr, 6.9 mL, 0.085 mmol) was added via calibrated gas volume. The tube was then sealed with a torch, thawed, and placed in a thermostated bath. Approximately 8−10 spectra were recorded at regular intervals during the course of the reaction, and the intensity of each peak was measured by integration versus the internal standard. The rate of the reaction was then plotted as an approach to equilibrium, as described previously.[30]

$(\eta^5\text{-}C_5Me_4H)_2Zr(CH_2CDMe_2)(D)$ (2). This compound was prepared in the same manner as **1**. Attempts to isolate solid samples produced

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an oil unsuited to elemental analysis. ^{1}H NMR (benzene-d_6): $\delta = 2.13$ (s, 6H, C_5Me_4H), 2.07 (s, 6H, C_5Me_4H), 1.99 (s, 6H, C_5Me_4H), 1.94 (s, 6H, C_5Me_4H), 5.11 (s, 2H, C_5Me_4H), −0.07 (s, 2H, CH_2CDMe_2), 1.03 (s, 6H, CH_2CDMe_2). ^{2}H (benzene): $\delta = 5.93$ (s, 1D, Zr-*D*), 2.23 (s, 1D, CH_2CDMe_2).

Cp*$_2$Zr(CH$_2$CH$_2$CH$_3$)(H). In the drybox, a J. Young NMR tube was charged with 7.0 mg (0.019 mmol) of Cp*$_2$ZrH$_2$, and 0.50 mL of benzene-d_6 was added, forming a clear solution. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. Via a 6.9-mL calibrated gas bulb, 52 Torr (0.019 mmol) of propylene was added at −196 °C. The solution was then thawed and the tube shaken. With shaking the solution turned from colorless to yellow. This compound decomposes in solution over the course of days at room temperature or during attempts to isolate it as a solid sample. ^{1}H NMR (benzene-d_6): $\delta = 1.94$ (s, 30 H, Cp*), −0.25 (m, 2H, $CH_2CH_2CH_3$), 1.86 (m, 2H, $CH_2CH_2CH_3$), 1.86 (t, $J = 7$ Hz, 3H, $CH_2CH_2CH_3$). For Cp*$_2$Zr(^{13}CH$_2$CH$_2$CH$_3$)(H), ^{13}C{^{1}H} NMR (benzene-d_6): $\delta = 55.15$ ($CH_2CH_2CH_3$), 20.98 ($CH_2CH_2CH_3$).

(η^5-C$_5$Me$_4$H)$_2$Zr(CH$_2$CH$_2$CH$_3$)(H). This compound was prepared in the same manner as **1** using 8.0 mg (0.024 mmol) of (η^5-C$_5$Me$_4$H)$_2$ZrH$_2$ and 70 Torr (0.026 mmol) of propylene. This compound decomposes in solution over the course of days at room temperature or during attempts to isolate it as a solid sample. ^{1}H NMR (benzene-d_6): $\delta = 2.26$ (s, 6H, C_5Me_4H), 2.14 (s, 6H, C_5Me_4H), 2.08 (s, 6H, C_5Me_4H), 1.98 (s, 6H, C_5Me_4H), 5.43 (s, 2H, C_5Me_4H), −0.60 (m, 2H, $CH_2CH_2CH_3$), 2.29 (m, 2H, $CH_2CH_2CH_3$), 0.94 (t, $J = 7$ Hz, 3H, $CH_2CH_2CH_3$). For (η^5-C$_5$Me$_4$H)$_2$Zr(^{13}CH$_2$CH$_2$CH$_3$)(H), ^{13}C{^{1}H} NMR (benzene-d_6): $\delta = 55.74$ ($CH_2CH_2CH_3$), 20.24 ($CH_2CH_2CH_3$).

Isomerization of Cp*$_2$Zr(^{13}CH$_2$CH$_2$CH$_3$)(H) and (η^5-C$_5$Me$_4$H)$_2$Zr(^{13}CH$_2$CH$_2$CH$_3$)(H) by ^{13}C NMR Analysis. In the drybox, a J. Young NMR tube was charged with 0.50 mL of a 0.166 M stock solution of metallocene in benzene-d_6. On the vacuum line, the solution was frozen and degassed with three freeze−pump−thaw cycles. While the solution was frozen in liquid nitrogen, $^{13}CH_2{=}CHCH_3$ was added to the tube via a 6.9-mL calibrated gas volume. The tube was sealed, rotated several times, and then placed in the temperature-calibrated NMR probe. Approximately 8−10 spectra were recorded at regular intervals during the course of the reaction. The intensity of each peak was determined by integration, and the kinetics were plotted as an approach to equilibrium.

Cp*(C$_5$H$_4$-CMe$_3$)Zr(CH$_2$CH$_2$CH$_3$)(H). This compound was prepared in the same manner as **1** using 6.8 mg (0.0196 mmol) of [Cp*(C$_5$H$_4$-CMe$_3$)ZrH$_2$]$_2$ and 52 Torr (0.0196 mmol) of propylene. This compound decomposes in solution over the course of days at room temperature or during attempts to isolate it as a solid sample. ^{1}H NMR (benzene-d_6): $\delta = 1.82$ (s, 15H, Cp*), 1.40 (s, 9H, C_5H_4-CMe_3), 5.32, 4.91, 4.88, 4.20 (m, C_5H_4-CMe$_3$), 5.94 (s, 1H, Zr-*H*), −0.50 (m, 2H, $CH_2CH_2CH_3$), 2.10 (m, 2H, $CH_2CH_2CH_3$), 1.07 (t, $J = 6$ Hz, 3H, $CH_2CH_2CH_3$). For Cp*(C$_5$H$_4$-CMe$_3$)Zr(^{13}CH$_2$CH$_2$CH$_3$)(H), ^{13}C{^{1}H} NMR (benzene-d_6): $d = 55.07$ ($CH_2CH_2CH_3$), 21.33 ($CH_2CH_2CH_3$).

Kinetics of β-Hydrogen Elimination. In the drybox, 0.50 mL of a 0.244 M stock benzene-d_6 solution of (CpR$_n$)$_2$ZrH$_2$ containing a known amount of ferrocene was charged into a J. Young NMR tube. On the vacuum line, isobutene was added via a calibrated gas volume. The tube was allowed to stand at room temperature for 1 h to ensure complete reaction. The tube was then cooled to −196 °C, and either 2-butyne (for Cp*$_2$Zr(CH$_2$CHMe$_2$)(H)) or 4,4-dimethyl-2-pentyne (for (η^5-C$_5$HMe$_4$)$_2$Zr(CH$_2$CHMe$_2$)(H)) was added via a calibrated volume. The tube remained frozen until its insertion into a precooled NMR probe. Approximately 10−15 spectra were recorded over regular intervals during the course of the reaction, and the intensity of each peak was measured by integration versus the internal standard. The rate of the reaction was then plotted, and the data were fitted using a least-squares analysis. Representative data for Cp*$_2$Zr(CH$_2$CHMe$_2$)(H) at 296 K: $k_{obs} = 2.8(4) \times 10^{-4}$ s^{-1} at [CH$_3$C≡CCH$_3$] = 0.244 M; $k_{obs} = 2.5(6) \times 10^{-4}$ s^{-1} at [CH$_3$C≡CCH$_3$] = 0.650 M; $k_{obs} = 3.1(5) \times 10^{-4}$ s^{-1} at [CH$_3$C≡CCH$_3$] = 1.10 M. For (η^5-C$_5$HMe$_4$)$_2$Zr(CH$_2$CHMe$_2$)(H) at 296 K: $k_{obs} = 5.4(2) \times 10^{-4}$ s^{-1} at [CH$_3$C≡CCCMe$_3$] = 0.061 M; $k_{obs} = 5.4(2) \times 10^{-4}$ s^{-1} at [CH$_3$C≡CCCMe$_3$] = 0.244 M; $k_{obs} = 5.4(2) \times 10^{-4}$ s^{-1} at [CH$_3$C≡CCCMe$_3$] = 0.976 M.

Cp$_2$Zr(CH$_2$CHMe$_2$)(Cl). In the drybox, a J. Young NMR tube was charged with 9.0 mg (0.035 mmol) of **3** and benzene-d_6 added. On the vacuum line, the tube was frozen in liquid nitrogen and degassed with three freeze−pump−thaw cycles. Via a calibrated gas volume, 108 Torr (0.040 mmol) of isobutene was added at −196 °C. The tube was thawed and rotated. With time, dissolution of **3** was observed with formation of a bright yellow solution. Attempts to isolate this material as a solid sample led instead to an intractable oil not suited to elemental analysis. ^{1}H NMR (benzene-d_6): $\delta = 6.24$ (s, 10H, C_5H_5), 0.968 (d, $J = 6.4$ Hz, 2H, CH_2CHMe_2), 2.20 (sept, $J = 6.5$ Hz, 1H, CH_2CHMe_2), 0.849 (d, $J = 6.5$ Hz, 6H, CH_2CHMe_2). ^{13}C NMR (benzene-d_6): $\delta = 110.94$ (η^5-C_5H_5), 50.27 (CH_2), 38.44 (CH_2), 13.79 ($CH(CH_3)_2$).

Cp$_2$Zr(CH$_2$CH$_2$CH$_2$CH$_3$)(Cl). In the drybox, a J. Young NMR tube was charged with 15.0 mg (0.058 mmol) of **3** and benzene-d_6 added. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. Via a calibrated gas bulb, 165 Torr (0.061 mmol) of 1-butene was added at −196 °C. The solution was then thawed and the tube shaken. With shaking, the white solid dissolved, forming a yellow solution. Attempts to isolate this material as a solid sample led instead to an intractable oil not suited to elemental analysis. ^{1}H NMR (benzene-d_6): $\delta = 5.77$ (s, 10H, C_5H_5), 1.10 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.58 (pent, $J = 7.2$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.37 (m, $J = 7.3$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.02 (t, $J = 7.3$ Hz, 3H, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (benzene-d_6): $\delta = 112.86$ (C_5H_5), 55.55 ($CH_2CH_2CH_2CH_3$), 37.16 ($CH_2CH_2CH_2CH_3$), 29.72 ($CH_2CH_2CH_2CH_3$), 14.38 ($CH_2CH_2CH_2CH_3$).

Cp$_2$Zr(CH$_2$CHDCH$_2$CH$_3$)(Cl). A sample was prepared in a manner identical to that described above with 35.0 mg (0.135) of **3**-*d*. {^{1}H}^{2}H NMR (benzene): $\delta = 1.57$ (s, 1D, $CH_2CDHCH_2CH_2CH_3$).

Cp$_2$Zr(CH$_2$CH$_3$)(Cl). In the drybox, a J. Young NMR tube was charged with 14.0 mg (0.054 mmol) of **3** and benzene-d_6 added. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. Via a 6.9-mL calibrated gas bulb, 250 Torr (0.092 mmol) of ethylene was added at −196 °C after passage through a −80 °C trap. The solution was then thawed and the tube shaken. With shaking, the white solid dissolved, forming a yellow solution. Attempts to isolate this material as a solid sample led instead to an intractable oil not suited to elemental analysis. ^{1}H NMR (benzene-d_6): $\delta = 5.76$ (s, 10H, C_5H_5), 1.09 (q, $J = 7.6$ Hz, 2H, CH_2CH_3), 1.44 (t, $J = 7.65$ Hz, CH_2CH_3). ^{13}C NMR (benzene-d_6): 111.57 (η^5-C_5H_5), 56.10 (CH_2), 14.70 (CH_3).

Cp$_2$Zr(CH$_2$CH$_2$D)(Cl). A sample was prepared in a manner identical to that described above with 57.0 mg (0.220) of **3**-*d*. {^{1}H}^{2}H NMR (benzene): $\delta = 1.38$ (s, 1D, CH_2CH_2D).

Cp$_2$Zr(CH$_2$CH$_2$CH$_3$)(Cl). In the drybox, a J. Young NMR tube was charged with 5.0 mg (0.014 mmol) of **3** and benzene-d_6 added. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. Via a calibrated gas bulb, 60 Torr (0.022 mmol) of $CH_2{=}CHCH_3$ was added at −196 °C. The solution was then thawed and the tube shaken. With shaking, the white solid dissolved, forming a yellow solution. Attempts to isolate this material as a solid sample led instead to an intractable oil not suited to elemental analysis. ^{1}H NMR (benzene-d_6): $\delta = 5.77$ (s, 10H, C_5H_5), 1.09 (m, 2H, $CH_2CH_2CH_3$), 1.50 (m, 2H, $CH_2CH_2CH_3$), 1.01 (t, $J = 7$ Hz, 3H, $CH_2CH_2CH_3$). For Cp$_2$Zr(^{13}CH$_2$CH$_2$CH$_3$)(Cl), ^{13}C NMR (benzene-d_6): $\delta = 58.72$ ($CH_2CH_2CH_3$).

Cp$_2$Zr(*cyclo*-C$_5$H$_9$)(Cl). In the drybox, a 25-mL round-bottom flask equipped with a stir bar was charged with 0.430 g (1.67 mmol) of **3**, and a 180° needle valve was attached. On the vacuum line, approximately 10 mL of Et$_2$O was added by vacuum transfer at −78 °C. While at −78 °C, 400 Torr of cyclopentene was added. The reaction was backfilled with argon and warmed to room temperature with stirring. Over the course of several hours, a clear yellow solution formed. The reaction was continued for 12 h, and then all volatiles were removed in vacuo. The reaction flask was transferred onto a swivel frit assembly and the yellow solid extracted with Et$_2$O. The Et$_2$O was removed in vacuo, leaving a yellow solid. The solid was recrystallized from Et$_2$O at −40 °C in the drybox freezer. Yield of product: 0.350 g (63.5%). ^{1}H NMR (benzene-d_6): $\delta = 5.79$ (s, 10H, C_5H_5), 1.59 (m, 1H, C_5H_9), 1.67 (m, 2H, C_5H_9), 1.46 (m, 2H, C_5H_9), 1.45 (m, 2H, C_5H_9), 1.92 (m, 2H, C_5H_9). Anal. Calcd for $C_{15}H_{19}Zr_1Cl_1$: C, 55.27; H, 5.87. Found: C, 54.97; H, 5.90.

$Cp_2Zr(CH_3)(CH_2CH_2CH_3)$. In the drybox, a J. Young NMR tube was charged with 5.0 mg (0.021 mmol) of $[Cp_2Zr(CH_3)(H)]_2$ and benzene-d_6 added. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. Via a 6.9-mL calibrated gas bulb, 60 Torr (0.022 mmol) of $^{13}CH_2{=}CHCH_3$ was added at −196 °C. The solution was then thawed and the tube shaken. With shaking, the white solid dissolved, forming a yellow solution. The sample was placed in the NMR probe and monitored by ^{13}C and ^1H NMR spectroscopy. This compound decomposes in solution over the course of several days at room temperature or during attempted isolation as a solid sample, and thus, elemental analysis was not possible. ^1H NMR (benzene-d_6): δ = 5.71 (s, 10H, C_5H_5), 0.113 (s, 3H, Zr-CH_3), 0.518 (m, 2H, CH_2CH$_2$-CH$_3$), 1.66 (m, 2H, CH$_2$CH_2CH$_3$), 1.03 (t, J = 6.8 Hz, 3H, CH$_2$CH$_2$-CH$_3$). For $Cp_2Zr(CH_3)(^{13}CH_2CH_2CH_3)$, ^{13}C NMR (benzene-d_6): δ = 57.72 ($CH_2CH_2CH_3$), 27.34 ($CH_2CH_2CH_3$).

Addition of *cis*-2-Butene to 3. Identification of 9. In the drybox, a J. Young NMR tube was charged with 14.0 mg (0.054 mmol) of **3** and benzene-d_6 added. On the line, the tube was degassed with three freeze−pump−thaw cycles. Via a calibrated gas volume, 220 Torr (0.081 mmol) of *cis*-2-butene was added at −196 °C. The tube was thawed and shaken. With time, the white solid dissolved, forming a clear yellow solution. ^1H NMR (benzene-d_6) for **9**: δ = 5.78 (s, 10H, C_5H_5), 1.27 (d, J = 6.9 Hz, 3H, CH(CH_3)CH$_2$CH$_3$), 1.22 (m, 2H, CH-(CH$_3$)CH_2CH$_3$), 1.72 (m, 1H, CH(CH$_3$)CH$_2$CH$_3$), 0.973 (t, J = 7.1 Hz, 3H, CH(CH$_3$)CH$_2$CH_3). ^{13}C NMR (benzene-d_6): δ = 112.50 (C_5H_5), 62.86 (*C*H(CH$_3$)CH$_2$CH$_3$), 33.46 CH(*C*H$_3$)CH$_2$CH$_3$), 22.74 (CH-(CH$_3$)*C*H$_2$CH$_3$), 15.74 (CH(CH$_3$)CH$_2$*C*H$_3$).

Addition of 1-Pentene to 9. In the drybox, a J. Young NMR tube was charged with 8.0 mg (0.031 mmol) of **3** and benzene-d_6 added. On the vacuum line, the tube was degassed with three freeze−pump−thaw cycles. Via a calibrated gas volume, 90 Torr (0.033 mmol) of *cis*-2-butene was added. The tube was sealed and the solution thawed. The tube was rotated until all solid had dissolved (∼3 h). The NMR spectrum was recorded to verify the disappearance of starting materials. The tube was again placed on the vacuum line, and via a calibrated gas volume, 90 Torr (0.033 mmol) of 1-pentene was added. The solution was thawed and the tube shaken. ^1H NMR spectra were then recorded in several intervals over the course of 24 h.

Preparation of 1-^{13}C-2-Heptyne. In the drybox, a 100-mL round-bottom flask equipped with stir bar was charged with 2.00 g (22.7 mmol) of [Li][C≡CCH$_2$CH$_2$CH$_2$CH$_3$], and a 180° needle valve was attached. On the vacuum line, the flask assembly was evacuated, and ∼30 mL of ammonia was condensed onto the white solid at −78 °C. Against an Ar counterflow, 3.18 g (22.7 mmol) of $^{13}CH_3I$ was added via syringe with stirring. The reaction mixture was warmed to −50 °C, and the clear, colorless solution was stirred, forming a white precipitate. The reaction was stirred for 2 h, after which time the reaction was warmed to 0 °C and the NH_3 allowed to escape via an oil bubbler. In air, 10 mL of water was added and the organic layer collected. The clear organic layer was dried over $MgSO_4$, followed by CaH_2. The product was identified as 1-^{13}C-2-heptyne by comparison to the ^1H and ^{13}C NMR spectra of the authentic material. Yield: 1.80 g (82.5%).

Preparation of 1-^{13}C-*cis*-2-Heptene. In the drybox, a 100-mL round-bottom flask equipped with a stir bar was charged with 3.67 g (14.5 mmol) of $Cp_2Zr(H)(Cl)$, and a 180° needle valve was attached. On the vacuum line, approximately 25 mL of Et_2O was added by vacuum transfer. Against an Ar counterflow at −80 °C, 1-^{13}C-2-heptyne was added via syringe. The reaction was warmed to room temperature and stirred for 2 days. With time, the white suspension turned into a cloudy yellow solution. The reaction was quenched at 0 °C by addition of 10 mL of H_2O. An additional 50 mL of water was added, and the organic layer was collected and dried over $MgSO_4$. Ether was removed by atmospheric distillation. The clear, colorless liquid product was then distilled from CaH_2 and then vacuum transferred from $LiAlH_4$. Yield: 0.340 g (24%). The product was characterized by comparison of the ^1H and ^{13}C NMR spectra with authentic samples.

Reaction of 3 with 1-^{13}C-*cis*-2-Heptene. In the drybox, a screw-capped NMR tube was charged with 10.0 mg (0.0394 mmol) of **3** and benzene-d_6 added. To the tube was added 45 μL of a 1.0 M stock solution of 1-^{13}C-*cis*-2-heptene in benzene-d_6. The tube was shaken and placed in the NMR probe. Spectra were recorded over the course of 44 h.

Hydrozirconation of *cis*-2-Butene and *cis*-2-Heptene: CH_3OD Quench. In the drybox, a J. Young NMR tube was charged with ∼25 mg of **3**, and then C_6H_6 and 10 μL of benzene-d_6 were added. On the vacuum line, the solution was frozen in liquid nitrogen and the tube evacuated. Via a calibrated gas volume, olefin was added to the tube at −196 °C. The solution was frozen and rotated continuously at room temperature for the 12 h. The solution was then frozen in liquid nitrogen, and 20 μL of CH_3OD was added via microsyringe. The tube was capped, thawed, and shaken. The yellow solution turned clear with formation of white precipitate. The $\{^1H\}^2H$ NMR spectrum was then recorded, and the amount of internally deuterated alkane versus terminally deuterated alkane was determined by integration.

Hydrozirconation of *cis*-2-Heptene: CH_3OD Quench. Identification of Internal Heptanes. A procedure identical to that described above was followed, except that after 1 h, the reaction mixture was passed through a syringe filter in the drybox to remove any unreacted **3**. The clear yellow solution was frozen at −196 °C, CH_3OD was added, the tube was capped, thawed, and shaken, and the $\{^1H\}^2H$ NMR spectrum was recorded.

Structure Determination for 8. A suitable fragment was cut from a single crystal of **8**, attached to a glass fiber, and centered on an Enraf-Nonius CAD-4 diffractometer under an 85 K stream of N_2 gas. Unit cell parameters were obtained from the setting angles of 25 high-angle reflections. Two equivalent data sets were collected and merged in $P2_12_12_1$. Three reference reflections were measured every 75 min to monitor crystal decay. The structure was solved using direct methods, and the difference Fourier maps were used to locate all missing atoms, including hydrogens. A total of 5917 data were refined to R = 0.0287 (GOF = 1.78).

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Supporting Information Available: ORTEP drawings showing the complete atom labeling schemes, cell and crystal packing diagrams, and tables of atomic coordinates, complete bond distances, and angles and anisotropic displacement parameters for **8**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request free of charge, by quoting the publication citation and the deposition number 114941.

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