Organometallics **2005,** *24,* 2789−2794

Experimental Evidence for γ-Agostic Assistance in β-Methyl Elimination, the Microscopic Reverse of α-Agostic Assistance in the Chain Propagation Step of Olefin Polymerization

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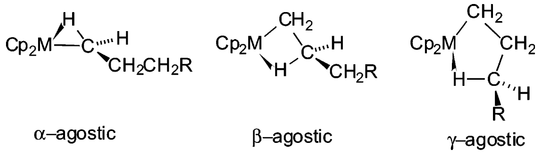
Received January 14, 2005

Isotopically labeled zirconocene methyl neopentyl complexes of the formula $(CpR_n)_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ are obtained via reaction of $LiCH_2C(CH_3)_2CD_3$ with $(CpR_n)_2Zr(CH_3)(Cl)$. Addition of $B(C_6F_5)_3$ to $(CpR_n)_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ results in β-methyl elimination, forming the ion-paired species $[(CpR_n)_2Zr(CH_3)][CH_3B(C_6F_5)_3]$ along with isotopologs of isobutene. The relative amounts of d_3- and d_0-isobutene afford the isotope effect for β-methyl elimination. For $Cp_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ ($Cp = (\eta^5\text{-}C_5H_5)$), a kinetic deuterium isotope effect of 1.40(2) has been measured at 23 °C. Comparable deuterium kinetic isotope effects have been observed for four other zirconocene methyl neopentyl compounds: $[Cp^*(C_5Me_4H)Zr]$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$), $[Cp^*_2Zr]$, [*rac*-(EBI)Zr] (EBI = ethylenebis(indenyl)), and [(THP)Zr] (THP = $1,2\text{-}(SiMe_2)_2(\eta^5\text{-}3,5\text{-}C_5H(CHMe_2)_2)(\eta^5\text{-}C_5H_3)$). The direction and magnitude of these effects are consistent with γ-agostic assistance in the transition state for β-methyl elimination, the microscopic reverse of α-agostic assistance in the transition state for olefin insertion into the Zr−methyl bond.

Introduction

Agostic interactions,[1] whereby a C−H σ bond forms a three-center, two-electron covalent bond to an electrophilic transition-metal center, are now ubiquitous in organometallic chemistry and have been identified in many catalytic reactions.[2] In metallocene-catalyzed α-olefin polymerizations computational studies have implicated α-agostic interactions as playing important roles in lowering the activation barriers for olefin insertion,[3] as well as increasing stereospecificity.[4] Experimental support for α-agostic assistance during olefin insertion into a metal−carbon bond was first achieved using Grubbs' isotopic perturbation of stereochemistry[5] for the catalytic hydrocyclization of trans-dideuterated α,ω-dienes with scandocene catalysts.[6−7] Studies by Brintzinger have identified α-agostic interactions (Chart 1) during the hydrodimerization of deuterated 1-hexene,[8] as well as during the polymerization of (*E*)- and (*Z*)-propene-d_1 with *ansa*-zirconocene catalysts.[9] Likewise, β-agostic ground-state structures have been identified in a number of group 3[10] and group 4 metallocene alkyls and are believed to be the catalyst resting states during polymerization.[11]

Chart 1



In addition to these interactions, γ-agostic structures have also been proposed in several Ziegler−Natta polymerization systems. Theoretical studies have identified γ-agostic interactions as the immediate kinetic products following olefin insertion[12] as well as possible resting states for the active species.[13] Experimental verifications of γ-agostic interactions are found in the

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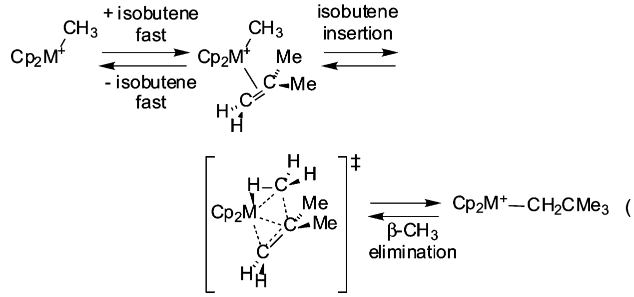
10.1021/om058002l CCC: $30.25

solid-state structures of $Cp^*_2YCH(SiMe_3)_2$, $Cp^*_2YN(SiMe_3)_2$,[14] and $RuCl_2(PPh_3)(N(SiMe_3)C(Ph)(NH(PPh_2)))$[15] and by NMR chemical shifts in tantalum carborane complexes.[16]

The microscopic reverse of isobutene insertion into a metal−methyl bond, namely β-methyl elimination from a neopentyl group (eq 1), is well suited to experimental detection of a γ-agostic interaction, because this transformation must access the same transition structure as the α-agostic-assisted reverse. Chain termination by β-methyl elimination has been identified in several olefin polymerization systems[17] and has also been observed in organoscandium complexes.[18] Additionally, Horton has described the reaction of $(CpR_n)_2Zr(CH_3)(CH_2CMe_3)$ with $B(C_6F_5)_3$, which results in formation of isobutene and $[(CpR_n)_2Zr(CH_3)][CH_3B(C_6F_5)_3]$ (CpR_n = (η^5-C_5H_5), (η^5-C_5Me_5)).[19] Because these metallocene systems are active olefin polymerization catalysts,[20] we felt that measurement of k_H/k_D for a suitably isotopically labeled neopentyl ligand of the complexes originally described by Horton would be a logical choice to identify a possible γ-agostic interaction accompanying β-methyl elimination. We describe herein the preparation of such zirconocene methyl neopentyl derivatives, along with measurements of the kinetic deuterium isotope effects that provide evidence for γ-agostic assistance in β-methyl elimination.



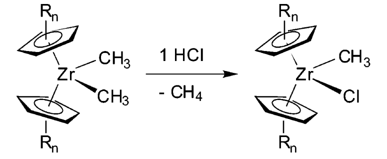
(1)

Results and Discussion

The strategy employed for the synthesis of isotopically labeled zirconocene methyl neopentyl complexes involved initial preparation of the zirconocene methyl chloride complexes followed by salt metathesis with labeled neopentyllithium, affording the desired zirconocene dialkyl. Preparation of $Cp_2Zr(CH_3)(Cl)$ was accomplished via known literature procedures,[21] whereas $Cp^*_2Zr(CH_3)(Cl)$, $Cp^*(C_5Me_4H)Zr(CH_3)(Cl)$, *rac*-(EBI)$Zr(CH_3)(Cl)$, and (THP)$Zr(CH_3)(Cl)$ were prepared via slow addition of 1 equiv of HCl to the corresponding dimethyl complex (eq 2).

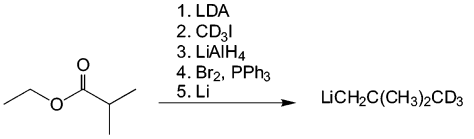
Table 1. Percentages of d_0-Isobutene, d_3-Isobutene, and d_6-Isobutene as a Function of Time for $Cp_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (1) Undergoing β-Methyl Elimination at 23 °C (Solvent Benzene)

	amt of isobutene (%)				
time (min)	d_0	d_3	d_6	total (mmol)	conversn (%)
2	26.7	73.3	<0.1	1.60×10^{-3}	2.5
10	26.1	73.9	<0.1	1.93×10^{-2}	29.9
18	26.1	73.9	<0.1	3.14×10^{-2}	48.6
26	26.2	73.8	<0.1	4.10×10^{-2}	63.6
45	27.2	72.5	0.2	4.94×10^{-2}	76.6
120	33.8	64.4	1.8	5.14×10^{-2}	79.7



(2)

Preparation of $LiCH_2C(CH_3)_2CD_3$ proceeded via methylation of ethyl isobutyrate with CD_3I followed by reduction of the ester to the alcohol via addition of lithium aluminum hydride (eq 3). Conversion of $HOCH_2C(CH_3)_2CD_3$ to the bromide was accomplished with addition of Br_2 in the presence of triphenylphosphine. Lithiation of the bromide in refluxing petroleum ether affords $LiCH_2C(CH_3)_2CD_3$ in modest yield. Addition of $LiCH_2C(CH_3)_2CD_3$ to the zirconocene methyl chloride complexes affords the desired dialkyl complexes. In this manner, $Cp_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**1**), $Cp^*_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**2**), $Cp^*(C_5Me_4H)Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**3**), *rac*-(EBI)$Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**4**), and (THP)$Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**5**) have been prepared in >95% isotopic purity.[22]



(3)

Slow cooling of a diethyl ether solution of **1** affords crystals that are suitable for X-ray diffraction (Table 1). The solid-state structure of **1** is shown in Figure 1 and displays a commonly observed coordination mode for zirconocene complexes. All of the hydrogen atoms have been located in the difference map and have been refined. No close hydrogen−metal contacts indicative of agostic interactions are observed in the solid-state structure of **1**.

Reaction of **1** with $B(C_6F_5)_3$ results in β-methyl elimination, initially forming d_3- and d_0-isobutene along with $[Cp_2Zr(CH_3)][CH_3B(C_6F_5)_3]$.[23] Monitoring the headspace of the reaction by GC/MS allows for quantification of each of the isotopologs produced. Control experiments

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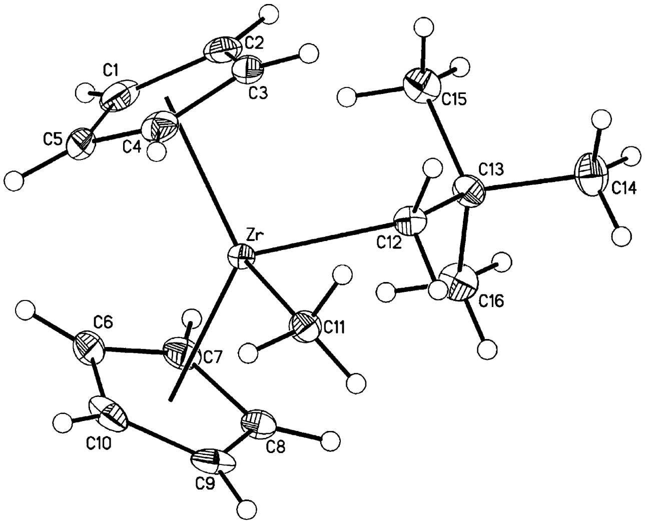
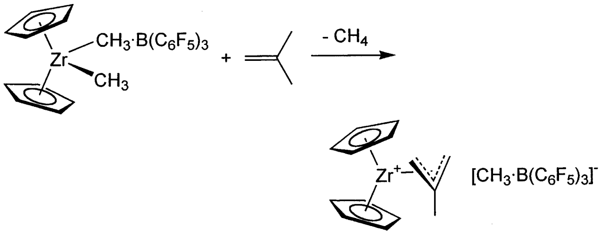


Figure 1. Molecular structure of $Cp_2Zr(CH_3)(CH_2CMe_3)$ (**1**) with 50% probability ellipsoids. Selected bond lengths (Å): Zr−Cent(1), 2.232; Zr−Cent(2), 2.234; Zr−C(11), 2.2980(13); Zr−C(12), 2.2719(12). Bond angles (deg): Cent(1)−Zr−Cent(2), 130.6; C(11)−Zr−C(12), 94.99. Cent(1) is the centroid 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).

to determine the detector response to different isotopologs of isobutene have been performed. Plots of detector response versus concentration of d_0- and d_8-isobutene ranging from 0.5 to 2.0 M have been constructed in order to determine the isotope effect, if any, on fragmentation. The detector response for d_0-isobutene (slope 416 responses/M; $R^2 = 0.992$) is almost identical with that for the d_8 isotopolog (slope = 410 responses/M; $R^2 = 0.989$).

At early reaction times for the β-methyl elimination of $\mathbf{1}\cdot B(C_6F_5)_3$, only d_0- and d_3-isobutene are detected, but as the reaction progresses d_6-isobutene gradually appears (Table 1). Competing insertion of d_3-isobutene into $[Cp_2Zr(CD_3)][CH_3B(C_6F_5)_3]$, followed by β-methyl elimination, accounts for formation of the d_6 isotopolog (Scheme 1). Allylic activation of the isobutene by $[Cp_2Zr(CH_3)][CH_3B(C_6F_5)_3]$ at longer reaction times (eq 4)



(4)

also complicates the observed values of the kinetic isotope effect.[19] As a result, all kinetic isotope effects reported are from early conversion, where the reaction is devoid of competing processes.

Scheme 1

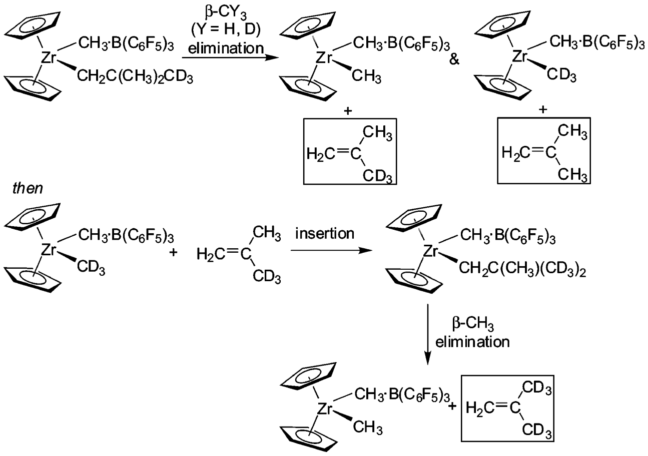


Table 2. Kinetic Deuterium Isotope Effects for β-Methyl Elimination for Zirconocene Methyl Neopentyl Derivatives 1−5

complex	k_H/k_D (23 °C)
$Cp_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**1**) + $B(C_6F_5)_3$	1.40(2)
$Cp^*{}_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**2**) + $B(C_6F_5)_3$	1.38(2)
$Cp^*(C_5Me_4H)Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**3**) + $B(C_6F_5)_3$	1.43(5)
rac-(EBI)$Zr(CH_3)CH_2C(CH_3)_2CD_3$ (**4**) + $B(C_6F_5)_3$	1.49(4)
(THP)$Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (**5**) + $B(C_6F_5)_3$	1.28(6)

From the ratio of d_3- and d_0-isobutene, a kinetic deuterium isotope effect (k_H/k_D) of 1.40(2) is observed for **1** at 23 °C. An isotope effect of this direction and magnitude is indicative of a transition state γ-agostic interaction during C−C bond breaking in the β-methyl elimination direction, in view of the very similar values (secondary $k_H/k_D = 1.3(1)$) established for the microscopic reverse, α-agostic assistance for olefin insertion into metal−alkyl bonds.[6−9] If a ground-state γ-agostic interaction, stronger than any transition-state γ-agostic interaction, were present, an inverse kinetic isotope effect would be expected.[24] The observed normal secondary isotope effect could, however, reflect an attenuation of the effect in the transition structure; i.e., the net isotope effect could represent a composite of a larger H vs D energy difference for the transition state and a ground-state EIE. While we cannot rule out this possibility, NMR chemical shifts suggest the lack of a substantial ground-state agostic interaction.[19]

The effect of temperature on the kinetic isotope effects during the β-methyl elimination reaction has been briefly investigated for **1** in toluene solution. At 5 °C, $k_H/k_D = 1.49(6)$, whereas at 35 °C, $k_H/k_D = 1.35(3)$.

Reaction of complexes **2**−**5** with $B(C_6F_5)_3$ also results in β-methyl elimination and formation of d_0- and d_3-isobutene. As with **1**, normal kinetic isotope effects are observed at 23 °C (Table 2), and for **1**−**4**, the value of the kinetic isotope effect is essentially invariant. However, for the doubly silylene linked **5**, a (marginally) smaller kinetic isotope effect of 1.28(6) is observed. In all cases, d_6-isobutene is observed at longer reaction times, indicative of reversible olefin insertion (Scheme 1).

Conclusions

The first experimental evidence for a γ-agostic interaction in the transition state for β-methyl elimination has been obtained for zirconocenium neopentyl cations. The magnitude and direction of the deuterium kinetic

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isotope effects are essentially independent of ancillary ligation. Comparing the values of the KIE's measured in insertion direction (α-agostic) with those for the β-methyl elimination direction (γ-agostic), ca. 1.3(1) vs 1.4(1), suggests that the reaction profile for this step is rather symmetric for eq 1, and the transition state is approximately halfway along the reaction coordinate.

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. Argon, dinitrogen, dihydrogen, and dideuterium gases were purified over columns of MnO on vermiculite and activated molecular sieves. Solvents for air- and moisture-sensitive reactions were stored under vacuum over titanocene. d_6-Benzene and d_8-toluene were purchased from Cambridge Isotope Laboratories. Both solvents were dried over $LiAlH_4$ and sodium and then stored over titanocene. Ethyl isobutyrate, lithium diisopropylamide, and bromine were purchased from Aldrich and used as received. Anhydrous hydrochloric acid was purchased from Aldrich and passed through a trap at −196 °C before use. Lithium turnings were purchased from Strem and stored under argon. Preparation of d_8-isobutene was accomplished via dehydration of $(CD_3)_3COD$ (Cambridge) with phosphoric acid. Preparation of *rac*-(EBI)$Zr(CH_3)_2$,[24,25] $Cp_2Zr(CH_3)(Cl)$,[21] $Cp^*_2Zr(CH_3)_2$, $Cp^*(C_5Me_4H)Zr(CH_3)_2$,[25,26] and (THP)$Zr(CH_3)_2$[26,27] was carried out as described previously.

NMR spectra were recorded on Bruker AM500 (500.13 MHz for ^1H, 76.77 for ^2H, 125.77 MHz for ^{13}C), JEOL Delta 400, and Varian Inova 500 spectrometers. All ^1H, ^2H, and ^{13}C NMR chemical shifts are relative to TMS using ^1H (residual), ^2H, or ^{13}C chemical shifts of the solvent as a secondary standard. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey.

GC-MS isotopic analyses were performed on a Hewlett-Packard 5972 mass spectrometer (Hewlett-Packard Co., Palo Alto, CA) equipped with a Hewlett-Packard Model 5980 Series II gas chromatograph. Separations were achieved on a 100% dimethylpolysiloxane capillary column (60 m, 0.32 mm i.d., 5 m film thickness; Rtx-1 Crossbond, Restek Corp., Bellefonte, PA). Electronic pressure control was used to maintain a constant column flow of 2 mL/min. Injections were performed in split mode with a 30:1 split ratio. The column temperature was programmed from 110 °C (2 min hold) to 185 °C at 25 °C/min and then to 230 °C at 50 °C/min for 2 min. The second ramp was used to clear benzene and toluene from the column.

The mass spectrometer was operated in the electron-impact mode with an electron energy of 70 eV at 15 A emission current. The electron multiplier was operated at 2012 V. The quadrapole was scanned from *m/z* 100 to 15 at a rate of 7.85 times per second. The detector response to isotopologs of isobutene was calibrated by making stock solutions of d_0- and d_8-isobutene and determining their response over a concentration range of 0.5−2.0 M and was found to be identical for both isotopologs. Furthermore, solutions of pure d_0- and d_3-isobutene were mixed and found to have additive responses. Determination of the amounts of d_0- (56 amu), d_3- (59 amu), and d_6-isobutene (62 amu) were integrated relative to an internal pentane standard (43 amu).

Preparation of d_3-Ethyl 2,2-Dimethylbutyrate. In the drybox, a three-necked round-bottom flask equipped with a magnetic stir bar was charged with 11.3 g (0.105 mol) of lithium diisopropylamide. A reflux condenser, inlet valve, and addition funnel were attached to the flask. On the Schlenk line, the flask assembly was purged with Ar for 10 min. Approximately 200 mL of THF was added via cannula, forming a brown solution. The addition funnel was charged with 12.0 g (0.103 mol) of ethyl isobutyrate and 10 mL of THF. The solution containing the ester was added slowly to the reaction mixture at −78 °C over the course of 10 min. The reaction mixture was stirred at −78 °C for 1 h. Into the addition funnel, 14.9 g (0.105 mmol) of CD_3I was charged, along with 10 mL of THF. The solution was dripped into the reaction mixture over the course of 15 min. The reaction mixture was maintained at −78 °C for an additional 30 min and then warmed to room temperature and stirred for 8 h. With time, a milky yellow-white reaction mixture formed. The reaction mixture was poured into 500 mL of brine, and the organic layer was collected. The aqueous layer was washed with three 50 mL portions of ether, and the organic layers were combined and dried over $MgSO_4$. The ether solution was filtered, and the solvent was removed via rotavap. The clear, colorless liquid was distilled at atmospheric pressure, yielding 7.03 g (52.4%) of product. The product was identified as d_3-ethyl 2,2-dimethylbutyrate by comparison of the ^1H and ^{13}C NMR spectra to those of an authentic sample.

Preparation of d_3-Neopentyl Alcohol. A three-necked, 500 mL round-bottom flask equipped with a magnetic stir bar was charged with 3.00 g (79.0 mmol) of $LiAlH_4$, and a reflux condenser, addition funnel, and gas inlet were attached. On the Schlenk line, the assembly was purged with Ar for approximately 20 min. Via cannula, approximately 200 mL of Et_2O was added. Into the addition funnel, 5.50 g (42 mmol) of d_3-ethyl 2,2-dimethylbutyrate was charged along with 50 mL of Et_2O. The ester solution was slowly dripped into the $LiAlH_4$ slurry over the course of 30 min. The reaction mixture was stirred overnight. The reaction was quenched via slow and careful addition of 3.0 mL of H_2O, followed by 15 mL of 15% NaOH and then finally 3 mL of H_2O. The organic layer was collected by filtration and was washed three times with H_2O. The organic layer was dried over Na_2SO_4 and the solvent removed by rotavap, leaving a clear liquid. The product was purified by atmospheric distillation, yielding 3.40 g (89%) of d_3-neopentyl alcohol. The product was identified as d_3-neopentyl alcohol by comparison of ^1H and ^{13}C NMR spectra to an authentic sample of $(CH_3)_3CCH_2OH$.

Preparation of d_3-Neopentyl Bromide. An argon-purged 250 mL three-necked flask equipped with a magnetic stir bar was charged with 9.42 g (35.9 mmol) of PPh_3. Approximately 100 mL of dimethylformamide was added by cannula. The flask was cooled to 0 °C, and 5.7 g (35.6 mmol) of Br_2 was added slowly via syringe. A cloudy white reaction mixture formed. The reaction mixture was warmed to room temperature and stirred for 30 min. Via syringe, a 50 mL solution of 3.00 g (32.9 mmol) of d_3-NpOH was added. With addition of alcohol, the solid in the flask dissolved. The reaction mixture was stirred at room temperature for 16 h. A distillation head was then attached to the flask, and the product was distilled out of the reaction mixture at 150 °C and atmospheric pressure. The product was washed with water three times and dried over Na_2SO_4, yielding 1.75 g (34.5%) of a clear liquid identified as d_3-NpBr by comparison to an authentic sample of $(CH_3)_3CCH_2Br$.

Preparation of d_3-NpLi. A 100 mL flask equipped with a stir bar was charged with fresh lithium turnings. Via cannula, approximately 50 mL of petroleum ether was added. Against an argon counterflow, 1.50 g (9.74 mmol) of d_3-NpBr was added via syringe. The reaction mixture was refluxed for 1 week, after which time a milky white slurry formed. The flask was transferred onto a swivel frit assembly and filtered. The petroleum ether was removed in vacuo, leaving 0.650 g (82.3%) of a white powder identified as d_3-NpLi, on the basis of comparison to an authentic sample of $(CH_3)_3CCH_2Li$.

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Preparation of $Cp_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (1). In the drybox, a 25 mL round-bottom flask was charged with 0.466 g (1.71 mmol) of $Cp_2Zr(CH_3)(Cl)$ and 0.139 g (1.71 mmol) of d_3-NpLi and attached to a swivel frit assembly. On the vacuum line, approximately 10 mL of Et_2O was added by vacuum transfer. The orange reaction mixture was warmed to room temperature and stirred for 16 h. The white precipitate was removed by filtration and washed three times with Et_2O. The solvent was removed in vacuo, leaving an orange oily solid. The oily solid was recrystallized from cold petroleum ether, yielding 0.400 g (75.3%) of a yellow powder, identified as $Cp_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ on the basis of comparison to literature data. $^2H\{^1H\}$ NMR: δ 1.02 ppm.

Preparation of $Cp^*_2Zr(CH_3)(Cl)$. In the drybox, a 50 mL flask was charged with 0.740 g (1.89 mmol) of $Cp^*_2Zr(CH_3)_2$ and attached to a calibrated gas volume. On the vacuum line, approximately 25 mL of petroleum ether was added by vacuum transfer, forming a clear solution. The 104 mL bulb was charged with 340 Torr (1.90 mmol) of anhydrous HCl. The gas was added to the flask at room temperature and the reaction mixture stirred for 3 days, over which time a white precipitate formed. The flask was transferred onto a swivel frit assembly and the solid collected by filtration and washed with petroleum ether. The solid was dried in vacuo, affording 0.450 g (58%) of $Cp^*_2Zr(CH_3)Cl$. ^1H NMR (d_6-benzene): δ 1.80 (s, 30H, Cp*), 0.00 (s, 3H, Zr−*Me*).

Preparation of $Cp^*_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (2). In the drybox a 25 mL round-bottom flask was charged with 0.200 g (0.485 mmol) of $Cp^*_2Zr(Me)Cl$ and 0.039 (0.485 mmol) d_3-NpLi. The flask was then attached to a fine swivel frit assembly. On the vacuum line, toluene was added by vacuum transfer. The reaction mixture was warmed to room temperature and stirred for 2 days. The solvent was removed in vacuo and the resulting yellow solid was extracted with petroleum ether. The solid was recrystallized from petroleum ether at −80 °C, affording 0.110 g (50.4%) identified as $Cp^*_2Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ on the basis of literature data.[19] ^2H NMR (benzene): δ 1.09 ppm.

Preparation of $Cp^*(C_5Me_4H)Zr(CH_3)(Cl)$. In the drybox, a 25 mL round-bottom flask equipped with a stir bar was charged with 0.290 g (0.767 mmol) of $Cp^*(C_5Me_4H)Zr(CH_3)_2$ and attached to a 43.48 mL calibrated gas volume. On the vacuum line, approximately 10 mL of petroleum ether was added by vacuum transfer. The gas bulb was charged with 330 Torr (0.767 mmol) of anhydrous HCl. The HCl was added to the solution at room temperature. The reaction mixture was stirred for 13 h, over which time a white precipitate formed. The flask was transferred onto a swivel frit and the white solid collected by filtration and washed with petroleum ether. The solid dried in vacuo, leaving 0.200 g (65.4%) of $Cp^*(C_5Me_4H)Zr(CH_3)(Cl)$. ^1H NMR (d_6-benzene): δ 1.81 (s, 15H, Cp*), 2.10 (s, 3H, $C_5\mathit{Me}_4H$), 1.92 (s, 3H, $C_5\mathit{Me}_4H$), 1.76 (s, 3H, $C_5\mathit{Me}_4H$), 1.45 (s, 3H, $C_5\mathit{Me}_4H$), 4.73 (s, 3H, $C_5Me_4\mathit{H}$), −0.02 (s, 3H, Zr−*Me*). ^{13}C NMR (d_6-benzene): 12.39 ($C_5\mathit{Me}_5$), 12.04, 12.11, 12.72, 12.82 ($C_5\mathit{Me}_4H$), 107.46 (C_5Me_5), 106.45, 105.59, 119.81 (C_5Me_4H), 2 peaks *not located*, 38.06 (Zr−*Me*). Anal. Calcd for $Zr_1C_{20}H_{31}Cl_1$: C, 60.34; H, 7.85. Found: C, 60.72; H, 8.29.

Preparation of $Cp^*(C_5Me_4H)Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (3). In the drybox, a 25 mL flask was charged with 0.140 g (0.351 mmol) of $Cp^*(C_5Me_4H)Zr(Me)(Cl)$ and 0.028 g (0.351 mmol) of d_3-NpLi. The flask was attached to a fine swivel frit assembly. On the vacuum line, approximately 10 mL of toluene was added by vacuum transfer. The reaction mixture was warmed to room temperature and stirred for 3 days, over which time a yellow solution and white precipitate formed. The toluene was removed in vacuo, and petroleum ether was added by vacuum transfer. The white precipitate was removed by filtration and the solvent removed in vacuo, leaving a yellow oil. Attempts to crystallize the oil by slow cooling of ether or petroleum ether solution were not successful. ^1H NMR (d_6-benzene): δ 1.80 (s, 15H, Cp*), 2.15 (s, 3H, $C_5\mathit{Me}_4H$), 2.09 (s, 3H, $C_5\mathit{Me}_4H$), 1.98 (s, 3H, $C_5\mathit{Me}_4H$), 1.85 (s, 3H, $C_5\mathit{Me}_4H$), 4.60 (s, 1H, $C_5Me_4\mathit{H}$), 1.12 (s, 6H, $Zr{-}CH_2C(\mathit{CH_3})_2(CD_3)$)), 0.21 (d, 1H, 10 Hz, $Zr{-}C\mathit{H}_2C(\mathit{CH_3})_2(CD_3)$), −0.02 (d, 1H, 10 Hz, $Zr{-}C\mathit{H}_2C(\mathit{CH_3})_2(CD_3)$)), −0.37 (s, 3H, Zr−*Me*). ^2H NMR (benzene): δ 1.10. Isolation as an oil prevented elemental analysis.

Preparation of *rac*-$(EBI)Zr(CH_3)(CH_2C(CH_3)_2CD_3)$ (4). In the drybox, a 25 mL round-bottom flask was charged with 0.150 g (0.376 mmol) of *rac*-$(EBI)Zr(CH_3)(Cl)$ and 0.031 g (0.376 mmol) of d_3-NpLi. The flask was attached to a medium swivel frit assembly. On the vacuum line, approximately 10 mL of Et_2O was added by vacuum transfer, and the mixture was warmed to room temperature. The reaction mixture was stirred for 24 h, over which time an orange solution and white precipitate formed. The white solid was removed by filtration and the solvent removed in vacuo, leaving an orange solid. The solid was dried in vacuo, affording 0.080 g of product (49.0%). ^1H NMR (d_6-benzene): δ −1.98 (d, 6 Hz, 1H, $C\mathit{H}_2C(CH_3)_2CD_3$), −0.02 (d, 6 Hz, 1H, $C\mathit{H}_2C(CH_3)_2CD_3$), −0.95 (s, 3H, $Zr{-}C\mathit{H}_3$), 0.87 (s, 6H, $Zr{-}CH_2C(C\mathit{H}_3)_2CD_3$), 2.65 (m, 2H, $C\mathit{H}_2CH_2$, EBI), 2.82 (m, 2H, $CH_2C\mathit{H}_2$, EBI), 5.55 (m, 1H, Cp, EBI), 5.63 (m, 1H, Cp, EBI), 5.76 (m, 1H, Cp, EBI), 6.40 (m, 1H, Cp, EBI), 6.8−7.4 (m, benzo, EBI). ^2H NMR (benzene): δ 0.85 ppm.

Preparation of $(THP)Zr(CH_3)(Cl)$. In the drybox, a 25 mL round-bottom flask was charged with 0.330 g (0.735 mmol) of $(THP)Zr(CH_3)_2$ and the flask attached to a 43.48 mL calibrated gas volume. On the vacuum line, petroleum ether was added by vacuum transfer and the solution warmed to room temperature. The gas bulb was charged with 314 Torr (0.735 mmol) of anhydrous HCl. The HCl was added at room temperature and the reaction mixture stirred for 3 days, over which time a white solid precipitated from solution. The precipitate was collected by filtration and washed with cold ether. The solid was dried in vacuo, affording 0.280 g (82%) of a white solid identified as $(THP)Zr(CH_3)(Cl)$. ^1H NMR (d_6-benzene): δ 0.348 (s, 3H, Me_2Si), 0.549 (s, 3H, Me_2Si), 0.791 (s, 3H, Me_2Si), 0.814 (s, 3H, Me_2Si), 0.161 (s, 3H, Zr−*Me*), 0.840 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 1.10 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 1.24 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 1.39 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 2.61 (sept, 7 Hz, 1H, $C\mathit{H}Me_2$), 2.91 (sept, 7 Hz, 1H, $C\mathit{H}Me_2$), 6.31 (m, 1H, Cp), 6.40 (m, 1H, Cp), 6.59 (m, 1H, Cp), 6.69 (m, 1H, Cp). ^{13}C NMR (d_6-benzene): δ −0.1865, −0.689, 3.59, 3.63 (Me_2Si), 31.62 ($Zr{-}\mathit{CH}_3$), 28.82, 28.97, 29.38, 29.60 ($CH\mathit{Me}_2$), 21.23, 21.00 ($\mathit{CH}Me_2$), 104.41, 111.18, 112.27, 114.65, 116.71, 128.68, 132.21, 133.74, 157.27, 160.03 (Cp). Anal. Calcd for $ZrC_{21}H_{33}ClSi_2$: C, 53.86; H, 7.10. Found: C, 52.72; H, 7.49.

Preparation of $THPZr(CH_3)(CH_2C(CH_3)_2CD_3)$ (5). In the drybox, a 25 mL round-bottom flask equipped with a magnetic stir bar was charged with 0.200 g (0.426 mmol) of $(THP)Zr(Me)(Cl)$ and 0.0345 g (0.426 mmol) of d_3-NpLi. The flask was attached to a fine swivel frit, and on the vacuum line 10 mL of Et_2O was added by vacuum transfer. The reaction mixture was warmed to room temperature and stirred for 24 h, over which time a yellow solution and white precipitate formed. The precipitate was removed by filtration and washed with several portions of ether. The solvent was removed in vacuo, leaving a dark sticky solid. Recrystallization from cold petroleum ether afforded 0.120 g (51.5%) of a white solid identified as $THPZr(CH_3)(CH_2C(CH_3)_2CD_3)$. ^1H NMR (d_6-benzene): δ 0.093 (s, 3H, Me_2Si), 0.378 (s, 3H, Me_2Si), 0.516 (s, 3H, Me_2Si), 0.528 (s, 3H, Me_2Si), 0.5750 (s, 6H, $Zr{-}CH_2C(C\mathit{H}_3)_2CD_3$), 0.127 (s, 2H, $Zr{-}C\mathit{H}_2C(CH_3)_2CD_3$), 0.944 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 1.07 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 1.25 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 1.42 (d, 7 Hz, 3H, $CH\mathit{Me}_2$), 2.62 (sept, 7 Hz, 1H, $C\mathit{H}Me_2$), 2.95 (sept, 7 Hz, 1H, $C\mathit{H}Me_2$), 6.34 (m, 1H, Cp), 6.45 (m, 1H, Cp), 6.63 (m, 1H, Cp), 6.72 (m, 1H, Cp). Anal. Calcd for $ZrC_{26}H_{41}D_3Si_2$: C, 61.59; H, 9.34. Found C, 60.92; H, 9.29.

General Procedure for Measurements of Isotope Effects. In a typical experiment, 20.0 mg (0.0645 mmol) of **1** was dissolved in 2.0 mL of a stock solution of benzene containing 0.2% (by weight) of pentane. Similarly, 36.0 mg (0.0703 mmol) of $B(C_6F_5)_3$ was dissolved in 1.0 mL of the stock benzene solution. In the drybox, the solution of **1** was charged into a 50 mL round-bottom flask equipped with a sidearm and a septum port. The sidearm of the flask was charged with the solution of $B(C_6F_5)_3$. The flask was placed in a thermostated bath of ethylene glycol and equilibrated to the desired temperature. The $B(C_6F_5)_3$ solution was added to the rapidly stirred zirconium solution, at which time a canary yellow solution formed. The reaction was monitored by withdrawing 100 μL of gas from the reaction vessel and injecting it into the GC/MS instrument.

Acknowledgment. This work has been supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER13431), by Exxon Chemicals America, and by the National Science Foundation (Grant No. CHE-0131180). We also thank Dr. Peter Green for assistance with GC/MS analysis and for helpful discussions.

Supporting Information Available: A CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 260138 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033. Structure factors are available from the authors via e-mail: xray@caltech.edu.

OM058002L