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0.500 M Methanol in Dodecane as Solvent. Run 1: 0.0212 M, 0.0163 mEinsteins, methoxydimethylsilane, 4.72×10^{-4} mmol, $\Phi = 0.0290$; product **4**, 1.48×10^{-3} mmol, $\Phi = 0.0907$; product **5**, 7.75×10^{-5} mmol, $\Phi = 0.0048$, conversion, 3.19%. **Run 2:** 0.0212 M, 0.0163 mEinsteins, methoxydimethylsilane, 5.20×10^{-4} mmol, $\Phi = 0.0319$; product **4**, 1.41×10^{-3} mmol, $\Phi = 0.0864$; product **5**, 6.32×10^{-5} mmol, $\Phi = 0.0039$, conversion, 3.13%.

Photolysis of *cis*-2-Butenylmethoxydimethylsilane (4) in Methanol. A solution of 102 mg (0.708 mmol) of butenylsilane **4** and 17.9 mg (0.14 mmol) of *n*-nonane (internal standard) in 40 mL of methanol was irradiated at 214 nm for 4 h, following the general procedure for direct photolyses. GC–MS analyses of aliquots after workup showed only three peaks with retention times and mass spectra corresponding to authentic samples **2**, **3**, and **4**. After a 1.8-h irradiation, GC analysis of an aliquot on column C gave 40% of reactant **1**, 12.6% of product **2**, and 9.94% of product **4**. Upon completion of the photolysis, GC analysis showed 55% of **1** had reacted to give 21% of **2** and 11% of **4**. The photolysis was diluted with 40 mL of pentane and washed twice with 40 mL of water, followed by drying over anhydrous sodium sulfate. The bulk of the pentane was distilled, and the reactant and photoproducts were isolated by preparative GC on column B at 72 °C. Each of the products was further identified by comparison of ^1H,^{13}C NMR, IR, and MS data to authentic samples.

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Registry No. **1**, 16054-12-9; **2**, 75732-19-3; **2**-*d*, 141556-99-2; **3**, 75732-22-8; **3**-*d*, 141557-00-8; **4**, 75732-23-9; **4**-*d*, 141557-01-9; **5**, 98582-83-3; **5**-*d*, 141557-02-0; methoxydimethylsilane, 18033-75-5; *cis*-1,4-dibromobut-2-ene, 18866-73-4.

OM920058P

THF Ring-Opening and H/D Exchange Reactions of $(C_5H_4Me)_2Zr(H)(THF)^+$. Evidence for Hydrogenolysis of Zr–Cp Bonds

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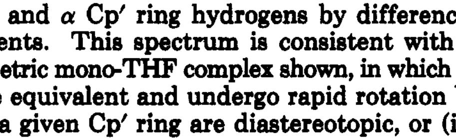
Summary: The cationic hydride $Cp'_2Zr(H)(THF)^+$ (**5**; Cp' = C_5H_4Me) reacts slowly in THF solution via THF ring opening to yield $Cp'_2Zr(O^nBu)(THF)^+$ (**7**). Hydride **5** undergoes rapid H/D exchange with D_2 at the Zr–H site, and slow H/D exchange at the β Cp'–H sites. No H/D exchange at the α Cp'-H or Cp'-CH_3 sites is detected. It is proposed that H/D exchange at the Zr–H site proceeds by a conventional σ-bond metathesis process and that exchange at the β Cp'-H site involves an intermediate (Cp')(methylcyclopentadiene)Zr species formed by D_2 addition across a Zr–Cp' bond. Exchange of H^- and $^nBuO^-$ ligands between Cp'_2Zr centers also leads indirectly to H/D exchange at the β Cp'-H sites of **7**.

Cationic d^0 alkyl complexes of general form $Cp_2Zr(R)^+$ (**1**) and $Cp_2Zr(R)(L)^+$ (**2**; L = labile ligand) are believed to be the active species in Cp_2ZrX_2-based Ziegler–Natta olefin polymerization catalysts.[1] Cationic hydrides $Cp_2Zr(H)^+$ (**3**) and $Cp_2Zr(H)(L)^+$ (**4**) are of interest in this context as they are the expected products of β-H elimination or hydrogenolysis reactions of **1** and **2** and hence of chain-transfer reactions in Cp_2ZrX_2-based catalysts. Hydrides of this type are also intermediates in catalytic olefin/pyridine coupling reactions and likely intermediates in olefin hydrogenation reactions.[1] We recently reported the synthesis of $Cp'_2Zr(H)(THF)^+$ (**5**; Cp' = C_5H_4Me) and its use in the synthesis of alkyls $Cp'_2Zr(CH_2CH_2R)(THF)^+$.[2] Complex **5** is one of the few cationic zirconium hydrides known, the others being the insoluble Cp analogue $Cp_2Zr(H)(THF)^+$, several phosphine hydrides $(C_5H_4R)_2Zr(H)(PR_3)_2^+$, and {ethylenebis(tetrahydroindenyl)}$Zr(H)(NMe_2Ph)^+$.[3,4] In this note we describe the THF ring opening and H/D exchange chemistry of **5**.

Results and Discussion

Synthesis and Solution Structure of $Cp'_2Zr(H)(THF)^+$ (5). Hydride **5** is prepared in situ in THF by reaction of $Cp'_2Zr(CH_3)(THF)^+$ (**6**) with H_2 (23 °C, 7 d, 1.2 atm, eq 1).[2,5] The low-temperature ^1H NMR spectrum of **5** (−40 °C) in THF-d_8 solution features a resonance at δ 5.72 characteristic of a terminal Zr–H, a single Cp'-CH_3 resonance, and three broad singlets (4/2/2 ratio) at δ 6.08 (α and β), 5.90 (β), and 5.53 (α), which have been assigned to the β and α Cp' ring hydrogens by difference NOE experiments. This spectrum is consistent with (i) the C_s-symmetric mono-THF complex shown, in which the Cp' rings are equivalent and undergo rapid rotation but the sides of a given Cp' ring are diastereotopic, or (ii) a C_s-symmetric bis(THF) complex.[6] At higher temperatures,



6 5 (1)

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(2) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. C. *Organometallics* **1989**, *8*, 2892.

(3) (a) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. (b) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289.

(4) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

(5) The counterion is BPh_4^- in all cases.

(6) (a) Exchange of THF and THF-d_8 is rapid on the chemical time scale so that resonances for coordinated THF are not observed. (b) Only the mono-THF complex is isolated. See ref 2.

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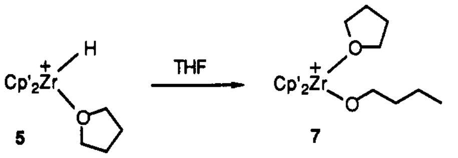
site exchange of the H^- and THF-d_8 ligands (which presumably occurs via intermolecular THF exchange) broadens the Cp′-H resonances, and a broad singlet is observed.

THF Ring Opening of 5. Hydride **5** rearranges slowly (weeks) at ambient temperature and more rapidly (48 h) at 60 °C to yield cationic *n*-butoxy complex $Cp'_2Zr(OCH_2CH_2CH_2CH_3)(THF)^+$ (**7**), which was isolated as a white crystalline solid (eq 2). The ^1H and ^{13}C spectra of THF-d_8 solutions of **7** exhibit the expected O–ⁿBu patterns, including resonances at δ 4.25 (^1H) and 76.8 (^{13}C) for the $Zr–OCH_2$ fragment. The ^1H NMR of **7** is essentially unchanged between 25 and −40 °C and contains a single $Cp-CH_3$ resonance and multiplets for the α (δ 6.22) and β (δ 6.25) Cp′ ring hydrogens (assignments confirmed by difference NOE experiments). This is consistent with rapid site exchange of the O–ⁿBu and THF ligands, which again presumably occurs via intermolecular THF exchange. Complex **7** was prepared independently by reaction of **6** with 1 equiv of *n*-butanol. Several cationic complexes related to **7** are known, including $Cp_2Zr(OR)(THF)^+$ (R = ᵗBu, ⁿBu, $CMePh_2$)[7] and $Cp^*{}_2Ti(OH)(H_2O)^+$.[8]

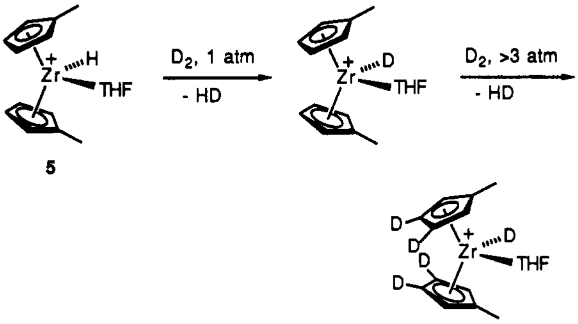


5 **7** (2)

Labeling experiments establish that the THF ring opening involves *net* nucleophilic attack by Zr–H at the THF α-carbon. Thermolysis of $Cp'_2Zr(H)(THF\text{-}d_8)^+$ (**5**-d_8) in THF-d_8 yields $Cp'_2Zr(OCD_2CD_2CD_2CD_2H)(THF\text{-}d_8)^+$ (**7**-d_{16}), the ^1H NMR spectrum of which exhibits a broad singlet for the CHD_2 group at δ 0.89, isotopically shifted as expected from the corresponding resonance (δ 0.95) for unlabeled **7**. Similarly, thermolysis of $Cp'_2Zr(D)(THF)^+$ in THF solution yields $Cp'_2Zr(OCH_2CH_2CH_2CH_2D)(THF)^+$ (^2H NMR: δ 0.98).

The ring-opening reaction leading to **7** is similar to the reactions of $Cp_2Zr(CH_2Ph)(THF)^+$ with the external nucleophiles PMe_2Ph or NMe_3, which yield $Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2PMe_2Ph)^+$ and $Cp_2Zr(CH_2Ph)(OCH_2CH_2CH_2CH_2NMe_3)^+$, respectively.[7b,9] The cationic phenyl complex $Cp_2Zr(Ph)(THF)^+$ initiates the ring-opening polymerization of THF by a similar process.[7b] These reactions manifest the potent Lewis acidity of the Cp_2ZrR^+ fragment which activates the coordinated THF for (intra or intermolecular) nucleophilic attack.[10]

H/D Exchange of 5. The reaction of **5** with D_2 results initially in H/D exchange of the Zr–H ligand (eq 3), which is complete in 24 h at 23 °C, 630 mm D_2 and is faster at higher D_2 pressures. This process is evidenced by the disappearance of the ^1H NMR Zr–H resonance and is accompanied by the formation of HD (δ 4.52, t, J_{HD} = 42.6 Hz). ^2H NMR experiments confirm deuterium incorporation at the Zr–H site. In a slower process at higher D_2 pressures, deuterium is also scrambled into the β Cp′ ring H positions of **5** (eq 3). This results in the reduction of the β Cp′-H resonances at δ 6.08 and 5.90 and is also accompanied by the formation of HD. There is no deuterium exchange at the α Cp′-H or Cp′-CH_3 positions as assessed by comparison of the intensities of the appropriate resonances to that of an internal standard. Complementary ^2H NMR experiments confirm incorporation of D in the Cp′-H sites; however, the ^2H NMR spectra were too broad at 25 and −40 °C to distinguish the α and β Cp′-H sites. The H/D exchange involving the β Cp′-H sites of **5** is too slow to be observed at D_2 pressures below ca. 3 atm at 25 °C and is unaffected by room light.



5 (3)

In a representative experiment, a THF-d_8 solution of $Cp'_2Zr(D)(THF)^+$ (**5**-d_1) was charged with 4.7 atm D_2 (9 equiv) and maintained at 25 °C for 8 d. ^1H NMR analysis revealed a decrease in the β Cp′-H resonances, the formation of HD, and the appearance of the Zr–H resonance, indicating that H/D scrambling between the β Cp′-H sites of **5**-d_1, the Zr–D site of **5**-d_1, and D_2 had occurred. At this point, 44% of the β Cp′-H sites were deuterated. After 26 d under these conditions, the scrambling process had reached equilibrium, and 85% of the β Cp′ sites and 68% of the Zr–H sites were deuterated. The higher D incorporation in the β Cp′-H site is consistent with the expected thermodynamic isotope effect which favors placement of D in the site with the higher vibrational frequency.[11]

The THF ring-opening reaction leading to **7** is competitive with the H/D exchange process involving the β Cp′-H site of **5**, as established by the appearance and growth of the resonances of **7** during the NMR monitoring experiments. For example, in the specific experiment discussed above, 17% conversion to **7** was observed after 8 d, and 33% conversion after 26 d. Interestingly, the ratio of the β Cp′-H to α Cp′-H signal intensities of **7** ("β/α intensity ratio") decreases during the course of the reaction, indicating that incorporation of deuterium into the β Cp′-H sites of **7** also occurs. In fact, at all points during the reaction, this ratio is equal to the β/α intensity ratio for **5**, i.e., the extent of D incorporation into the β Cp′-H sites of **5** and **7** is equal. As **7** does not undergo H/D exchange with D_2 in the absence of **5**,[12] the observed incorporation

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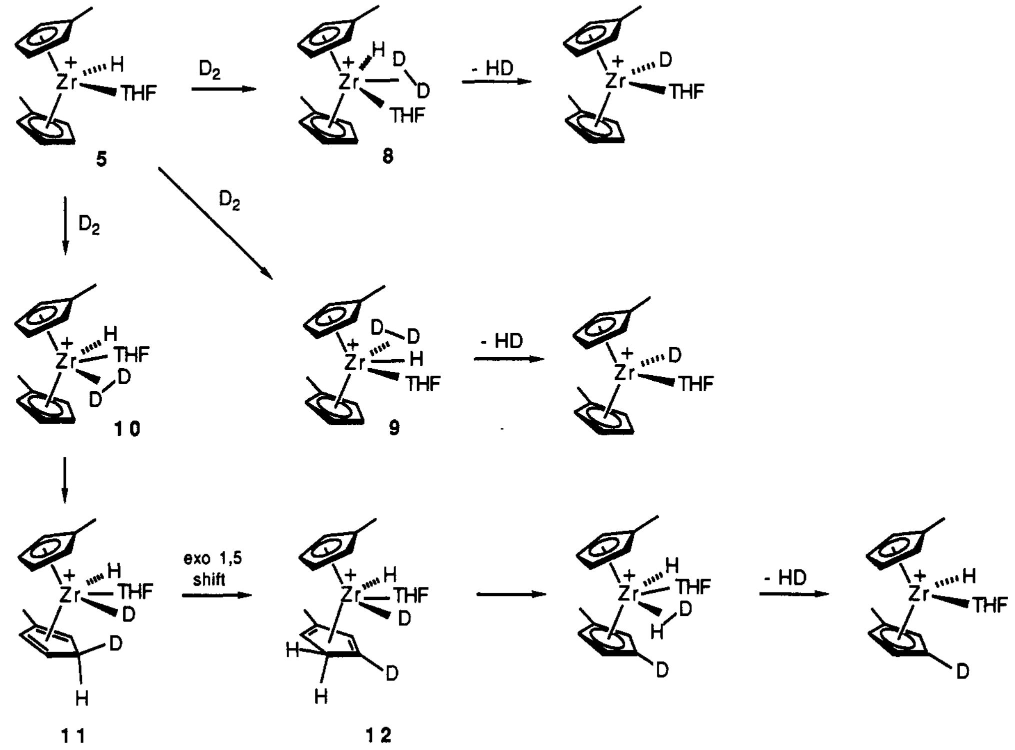
[9] (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

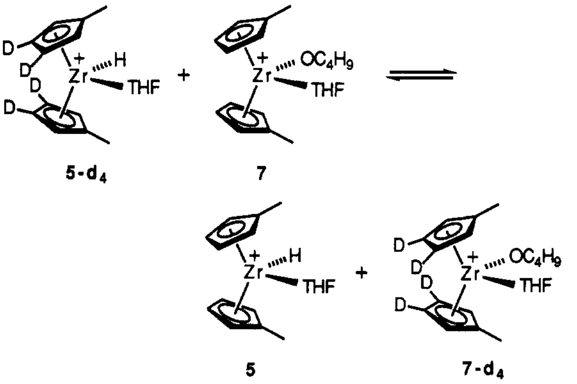
[10] For reviews and leading references to metal or other Lewis-acid-mediated THF ring-opening reactions, see: (a) Penczek, S.; Kubissa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1. (b) DeShong, P.; Sidler, D. R. *J. Org. Chem.* **1988**, *53*, 4892. (c) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124.

[11] (a) The equilibrium constant *K* for the net exchange of a single D between β Cp′-H and Zr–H sites, $(C_5H_4Me)(Cp')Zr(D)(THF)^+ \rightleftharpoons (C_5H_3DMe)(Cp')Zr(H)(THF)^+$ $K_{eq} = K$, is given by $K = 4\exp\{(hc/2kT)(\nu_{C-H} - \nu_{C-D} - \nu_{Zr-H} + \nu_{Zr-D})\}$, where the leading 4 is the statistical factor, and the ν values are in units of reciprocal centimeters.[11b,c] Using $\nu_{C-H} = 3000\ cm^{-1}$, $\nu_{C-D} = 2142\ cm^{-1}$, $\nu_{Zr-H} = 1390\ cm^{-1}$, and $\nu_{Zr-D} = 990\ cm^{-1}$ (values from ref 2), $K = 12$. *K* may also be expressed in terms of the mole fraction *y* of H in the β Cp′–H sites and the mole fraction *z* of H in the Zr–H site:[11d] $K = \{4y^3(1-y)z\}/\{y^4(1-z)\}$. Using the observed equilibrium mole fractions $y = 0.15$, $z = 0.32$ in this equation yields $K = 11$, in good agreement with the value estimated from the vibrational data. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper: New York, 1987; p 225. (c) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225. (d) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897, and accompanying supplementary material.

Scheme I



of D into **7** must occur indirectly, most likely by the ligand redistribution process in eq 4. This proposal is supported



(4)

by the observation that mixture of $(C_5H_2D_2Me)_2Zr(OCD_2CD_2CD_2CD_3)(THF\text{-}d_8)^+$ (**7**-d_{19}; 100% D-labeled in the β-Cp′-H sites) with unlabeled **5** (THF-d_8), at concentrations similar to those used in the D_2 reactions, results in complete scrambling of H^- and $^nBuO^-$ ligands between labeled and unlabeled Cp'_2Zr centers within 1 d at 25 °C. Analogous ligand redistribution reactions have been observed for other $Cp_2Zr(X)(L)^+$ complexes.[13]

H/D Exchange Mechanisms. Several mechanisms have been identified in the H_2 reactions of d^0 Cp_2M hydrides and alkyls.[14] The simplest and probably most common pathway is the σ-bond metathesis process in which direct hydrogenolysis of M–R or M–H bonds occurs via a four-center transition state. There is also evidence that addition of H_2 across M–Cp bonds to yield reactive d^0 Cp(cyclopentadiene)M^{IV} species occurs in some systems.[15] Indirect processes involving initial formation of d^2 (pentamethylcyclopentadiene)(Cp*)M^{II} species (via migration of Zr–H to a Cp* ligand) followed by oxidative addition of H_2 have been implicated for $(C_5Me_5)_2Zr$ systems.[16] The reslults described above suggest that the first two processes may be important in the H/D exchange chemistry of $Cp'_2Zr(H)(THF)^+$, as summarized in Scheme I.

In Scheme I, attack of D_2 at the central site of **5** (to yield **8**), or at the lateral site cis to the Zr–H ligand (to yield **9**), followed by σ-bond metathesis leads to H/D exchange of the Zr–H site. Attack of D_2 at the lateral site cis to THF leading to **10** is also possible but cannot lead to direct H/D exchange of Zr–H without loss of THF. In this case, addition of D_2 across a Zr–Cp′ bond may occur, leading to diene dihydride species **11**. Reversible 1,5 shifts of the exo H of **11** to yield, e.g., **12**, followed by HD elimination, would lead to scrambling of D into the β Cp′–H sites as shown. There is no *direct* exchange between the Zr–H and β Cp′-H sites of **5**. The observed *net* exchange of H from the β Cp′-H sites to the Zr–D site in the reaction of **5**-d_1 with D_2 occurs indirectly via σ-bond metathesis of Zr–D with HD.

There is no obvious reason for the remarkable regiospecificity of this exchange process (complete exchange of β Cp′-H sites and no detectable exchange of α Cp′-H sites). However, incorporation of D in an α Cp′-H site (via processes of the type in Scheme I) would require intermediates such as **13**, which may be sterically disfavored, and which contain a 1-methyl-1,3-cyclopentadiene ligand which in free/nonligated form is less stable than the 2-methyl-1,3-

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(12) The NMR spectrum of **7** (THF-d_8) under 4.7 atm D_2 was unchanged after 14 d at 25 °C.

(13) (a) Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383. (b) See footnote 29 in: Wang, Y.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406.

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(15) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65.

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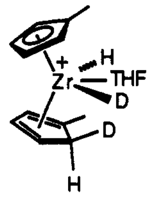

13

cyclopentadiene ligand in 11 (in free form).[17] Exchange processes involving (i) direct migration of Zr–D to a Cp′ ring to form a d^2 (Cp′)(methylcyclopentadiene)$Zr^{II}(THF)_n$ species or (ii) initial bimolecular loss of HD and formation of reactive, dinuclear μ-(η^5,η^1-fulvene) species do not appear to be important in this system because no H/D exchange between the Zr–D and β Cp′-H sites is observed for 5-d_1 in the absence of D_2.[18,19]

Experimental Section

All manipulations were performed under an N_2 atmosphere or under vacuum using a Vacuum Atmospheres drybox or a high-vacuum line. THF and THF-d_8 were purified by distillation from Na/benzophenone, stored in evacuated bulbs, and vacuum-transferred to reaction flasks or NMR tubes. NMR spectra were obtained on Bruker AC-300 or AMX-360 instruments. ^1H and ^{13}C chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. Elemental analyses were performed by E&R Microanalytical Laboratory Inc. $[Cp'_2Zr(CH_3)(THF)][BPh_4]$ (6) was prepared as described previously.[13b] All spectra contain normal BPh_4^- resonances.[2]

$[Cp'_2Zr(H)(THF)][BPh_4]$ (5). The preparation and complete characterization of this complex have been described previously.[2] ^1H NMR (25 °C, THF-d_8): δ 6.10–5.50 (br s, 8 H, C_5H_4Me), 5.88 (br s, 1 H, Zr-H), 2.21 (s, 6 H, Cp-CH_3). ^1H NMR (−40 °C, THF-d_8): δ 6.08 (s, 4 H, α,β Cp′-H), 5.90 (s, 2 H, β Cp′-H), 5.72 (s, 1 H, Zr-H), 5.53 (s, 2 H, α Cp′-H), 2.24 (s, 6 H).

$[Cp'_2Zr(OCH_2CH_2CH_2CH_3)(THF)][BPh_4]$ (7). A 100-mL glass bomb was charged with $[Cp'_2Zr(CH_3)(THF)][BPh_4]$ (6; 570 mg, 0.87 mmol), THF (50 mL, transferred at −78 °C), and H_2 (1 atm at −196 °C, 3.9 atm at 25 °C). The bomb was sealed, warmed to 25 °C, and stirred for 4 d. A pale-straw-colored solution of 5 formed. The pressure of the reaction vessel was reduced to 0.07 atm, and the solution was heated at 60 °C for 6 d. The resulting yellow solution of 7 was degassed and filtered to remove a small amount of colorless solid. The filtrate was evaporated in vacuo, yielding an off-white waxy solid. The crude product was dissolved in a small amount of THF, and hexane was added until a thick white slurry was obtained. The slurry was refrigerated overnight and filtered, and the resulting solid was washed with hexane and dried in vacuo to afford 7 as a white solid (310 mg, 50%). ^1H NMR (25 °C, THF-d_8): δ 6.25 (m, 4 H, β Cp′-H)), 6.22 (m, 4 H, α Cp′-H), 4.25 (t, J = 7 Hz, 2 H, OCH_2), 2.12 (s, 6 H, Cp′-CH_3), 1.56 (m, 2 H, OCH_2CH_2), 1.33 (m, 2 H, $OCH_2CH_2CH_2$), 0.95 (t, J = 7.5 Hz, 3 H, $O(CH_2)_3CH_3$). ^{13}C NMR (25 °C, THF-d_8): δ 131 (Cp′ ipso), 117 (Cp′), 115 (Cp′), 76.8 (OCH_2), 36.8 (OCH_2CH_2), 19.8 ($OCH_2CH_2CH_2$), 14.6 (Cp′-CH_3), 14.2 ($O(CH_2)_3CH_3$). Anal. Calcd for $C_{44}H_{51}BO_2Zr$: C, 74.02; H, 7.20. Found: C, 73.59; H, 7.26.

$[Cp'_2Zr(OCD_2CD_2CD_2CD_2H)(THF\text{-}d_8)][BPh_4]$ (7-d_{16}). A THF-d_8 solution of 5 in a sealed NMR tube was warmed at 60 °C for 2 d. A ^1H NMR spectrum confirmed >95% conversion to 7-d_{16} (95% NMR scale). ^1H NMR: δ 6.25 (m, 4 H, Cp′-H), 6.22 (m, 4 H, Cp′-H), 2.11 (s, 6 H, Cp′-CH_3), 0.89 (br s, 1 H, $ZrO(CD_2)_3CD_2H$).

Assignment of α and β Cp′-H Resonances of 5 and 7. Homonuclear ^1H difference NOE measurements for 5 were carried out at −40 °C using the Bruker program NOEDIFF. The spectrum obtained with single-frequency irradiation of the Cp′-CH_3 resonance was quantitatively compared to a spectrum obtained under identical conditions, but with the decoupler offset 1965 Hz downfield. A total of 32 transients (90° pulse, 2-min recycle time) were accumulated with alternation of the decoupler frequency every eight pulses. A 4.9% enhancement in the intensity of the δ 5.53 resonance and a 2.9% enhancement of the δ 5.90 resonance were observed. Therefore, these resonances were assigned to the α and β Cp′-H's, respectively.

Difference NOE measurements for 7 were carried out at 25 °C using the same procedure. In this case spectra obtained with irradiation of the Cp′-CH_3 resonance or at 2459 Hz downfield of this resonance were compared. A 6.3% enhancement in the intensity of δ 6.22 resonance and a 2.7% enhancement of the δ 6.25 resonance were observed. On this basis these resonances were assigned to the α and β Cp′-H's, respectively.[20]

H/D Exchange of 5. Solutions of 5 or $Cp'_2Zr(D)(THF)^+$ (5-d_1) were sealed in NMR tubes under D_2 (0–4.7 atm) and maintained at 25 °C. H/D exchange and formation of 7 were monitored by low-temperature ^1H NMR (−40 °C). The low temperature is required to distinguish the α and β Cp′-H sites of 5.

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[17] (a) Mclean, S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2329. (b) Stille, J. R.; Grubbs, R. H. *J. Org. Chem.* **1989**, *54*, 434.

[18] Scheme I provides a *simple* explanation of our observations. It is also possible that H/D exchange of β Cp′-H sites occurs via 8 and 9; i.e., 8 or 9 could also undergo addition of D_2 across a Zr–Cp bond, leading to intermediates analogous to 11 but with THF in a lateral position. Conversely, it is also possible that H/D exchange of the Zr–H site occurs indirectly via loss of HD from intermediate 11 (from methylcyclopentadiene and Zr–H). The more detailed studies required to distinguish these possibilites are hindered by the competing THF ring-opening and ligand redistribution reactions discussed in the text.

[19] Martin et al. observed that the hydrogenolysis product of $Cp'_2Ti(allyl)$ undergoes regiospecific H/D exchange at the β Cp′ sites; however, the organometallic species involved were not identified. Martin, H. A.; Van Gorkom, M.; De Jongh, R. O. *J. Organomet. Chem.* **1972**, *36*, 93.

[20] (a) In contrast, NOE experiments by Newmark et al. establish that the α Cp′-H signal of Cp'_2ZrMe_2 is downfield of the β Cp′-H signal. We have confirmed this result. Newmark, R. A.; Boardman, L. D.; Siedle, A. R. *Inorg. Chem.* **1991**, *30*, 853. (b) See also: Davis, J. H.; Sun, H.; Redfield, D.; Stucky, G. D. *J. Magn. Reson.* **1980**, *37*, 441.