Alkyl Substituent Effects on Reductive Elimination Reactions in Zirconocene Alkyl Hydride Complexes. Manipulation of the Alkyl Steric Environment Allows the Synthesis of a Zirconocene Dinitrogen Complex

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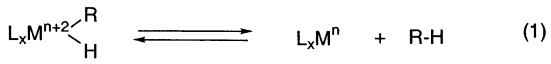
The rate of reductive elimination as a function of alkyl ligand has been measured for a series of zirconocene alkyl hydride complexes, Cp*Cp″Zr(R)H (Cp* = η^5-C_5Me_5, Cp″ = η^5-C_5H_3-1,3-$(SiMe_3)_2$, R = CH_3, $CH_2(CH_2)_2CH_3$, $CH_2(CH_2)_6CH_3$, $CH_2{}^cC_6H_{11}$, CH_2CHMe_2, CH_2CMe_3), where the steric disposition of the alkyl ligand has been systematically varied. The rate of reductive elimination increases modestly as the steric bulk of the alkyl ligand is increased. This trend is attributed to ground state destabilization arising from unfavorable steric interactions between the alkyl ligand and the cyclopentadienyl substituents. The effect is magnified when more voluminous cyclopentadienyl ligands are incorporated into the metallocene framework. Thus, the Cp*Cp‴Zr(R)H (Cp‴ = η^5-C_5H_2-1,2,4-$(SiMe_3)_3$, R = CH_3, $CH_2(CH_2)_2CH_3$, $CH_2(CH_2)_6CH_3$) series of alkyl hydride complexes lose alkane more readily than the corresponding Cp*Cp″Zr(R)H complexes. In addition, the rate of reductive elimination has also been examined for Cp*Cp″Zr(Ph)(H) and Cp*Cp″Zr(CH_2Ph)H (Ph = C_6H_5) and is slower than the alkyl hydride series. The sluggish rates of reductive elimination are a result of ground state stabilization imparted by a strong zirconium-phenyl bond and by η^2 coordination of the benzyl ligand, respectively. This interaction, along with the solid state structure of Cp*Cp″Zr(CH_3)H, has been characterized by X-ray diffraction. The kinetic data led to the synthesis of Cp*$_2$Zr(CH_2CMe_3)H, which undergoes reductive elimination of alkane and coordination of dinitrogen.

Introduction

Reductive elimination of alkane from a transition metal alkyl hydride is one of the fundamental transformations in organotransition metal chemistry and constitutes a key bond-forming step in numerous catalytic cycles (eq 1).[1] The microscopic reverse, oxidative addition of a carbon−hydrogen bond, has attracted considerable interest for its utility in alkane activation.[2] Alkane reductive elimination reactions with late transition metal compounds are quite common[3] and have been the subject of numerous mechanistic[4] and computational studies.[5]



(1)

Early transition metal reductive elimination reactions, although known for quite some time, have been studied less thoroughly. Schwartz and co-workers described ligand-induced reductive elimination, whereby addition of a phosphine ligand to $Cp_2Zr(R)H$ (Cp = η^5-C_5H_5; R = $CH_2C_6H_{11}$) triggered loss of alkane and formation of $Cp_2Zr(PR_3)_2$.[6] More recently, Ashe observed a similar phenomenon upon addition of PMe_3 to boratabenzene-ligated zirconium(IV) dialkyl complexes.[7] Nitrogen donors such as (dimethylamino)pyridine (DMAP)[8] and acetylenes[9] have also been shown to induce reductive elimination of alkane and dihydrogen, respectively, in zirconocene complexes. Legzdins has also reported ligand-induced reductive elimination in piano-stool tungsten aryl hydride complexes upon addition of isocyanides and organic carbonyls.[10] Ligand-induced reductive elimination has also been implicated in the stoichiometric preparation of cyclic β-phosphino imines with zirconium[11] as well as in the titanium-

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(2) For a recent review see: Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.
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(8) Van Wagenen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495.
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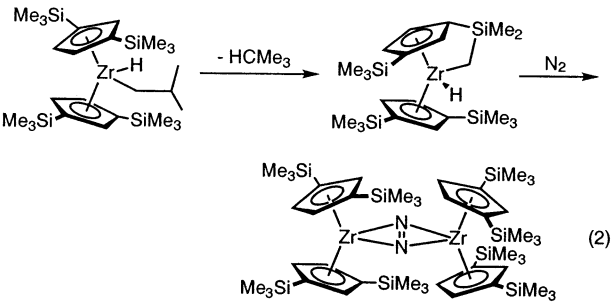
catalyzed ene reaction[12] and in the reductive cyclization of enones.[13]

Examples of alkane reductive elimination reactions that proceed thermally, without addition of exogeneous ligands, have been described for metallocenes of groups 4, 5, and 6. For example, $Cp^*_2Zr(CH_2CHMe_2)H$[14] ($Cp^* = \eta^5$-C_5Me_5) and $(CpR_5)_2W(CH_3)H$[15] (R_n = Me or H) lose alkane upon thermolysis. More recently, Parkin has observed thermal reductive elimination of dihydrogen in an *ansa*-tantalocene trihydride complex[16] and conducted a detailed mechanistic investigation into the nature of this reaction in related *ansa*-molybdenocene and *ansa*-tungstocene dihydrides and alkyl hydrides.[17] Choukroun[18] and Teuben[19] have also observed bimetallic reductive eliminations for the group 4 metals resulting in cyclopentadienyl ligand and dinitrogen activation, respectively.

Recent work from our laboratory has focused on the application of early transition metal alkane and dihydrogen reductive elimination reactions to the activation of small molecules such as elemental phosphorus[20] and dinitrogen.[21] For group 4 metallocene complexes, we discovered that sterically demanding cyclopentadienyl substituents such as [$SiMe_3$] groups are effective in promoting alkane reductive elimination under mild conditions.[21] Mechanistic studies on the zirconocene isobutyl hydride complex $Cp''_2Zr(CH_2CHMe_2)H$ ($Cp'' = \eta^5$-C_5H_2-(1,3-$SiMe_3$)$_2$) revealed that dinitrogen activation occurred from a zirconocene cyclometalated hydride rather than from direct reductive elimination of alkane (eq 2).

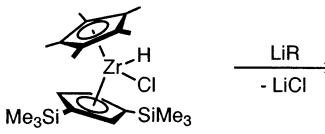


(2)

With an understanding of how cyclopentadienyl substituents influence the rate of reductive elimination, we became interested in learning how the alkyl ligand could be manipulated to control the rate of alkane loss. Such information could be used to design new zirconocene alkyl hydrides that undergo facile reductive elimination to form cyclometalated zirconocene hydrides that are reactive toward dinitrogen and other small molecules. Few studies, particularly in early transition metal chemistry, have focused on the effect of alkyl ligand on the rate of reductive elimination. Seminal studies by Halpern on square-planar bis-phosphine platinum alkyl hydride complexes demonstrated accelerated rates of alkane loss with increased size of the platinum alkyl.[22] Similar observations were made with related bis-neopentyl platinum phosphine complexes[23] and have also been noted in palladium,[24] rhodium,[25] and gold compounds.[26] In this report we describe a systematic study of the effect of alkyl ligand on the rate of reductive elimination in zirconocene alkyl hydride complexes. Application of our data has allowed the synthesis of a zirconocene dinitrogen complex by reductive elimination.

Results and Discussion

Preparation and Characterization of Zirconocene Alkyl Hydride Complexes. Synthesis of the desired zirconocene alkyl hydride complexes proceeded in a straightforward manner by addition of the appropriate alkyllithium to the zirconocene hydrido chloride complex Cp*Cp″Zr(H)Cl (**1**).[27] Initial studies focused on the preparation of a series of alkyl hydride complexes where the steric disposition of the alkyl ligand could be systematically varied. Thus, Cp*Cp″Zr(CH_3)H (**2**), Cp*Cp″Zr($CH_2(CH_2)_2CH_3$)H (**3**), Cp*Cp″Zr($CH_2(CH_2)_6CH_3$)H (**4**), Cp*Cp″Zr($CH_2{}^cC_6H_{11}$)H (**5**), and Cp*Cp″Zr(CH_2CMe_3)H (**7**) were synthesized and isolated in approximately 70% yield (eq 3). One exception



(3)

1

2: R = CH_3
3: R = $CH_2CH_2CH_2CH_3$
4: R = $CH_2(CH_2)_6CH_3$
5: R = $CH_2{}^cC_6H_{11}$
7: R = CH_2CMe_3
8: R = CH_2SiMe_3
9: R = C_6H_5
10: R = CH_2Ph

is the preparation of **2**. Monitoring the reaction in situ by ^{1}H NMR spectroscopy revealed a relatively clean alkylation reaction upon addition of $LiCH_3$. However a small (~5−10%) amount of a blue, paramagnetic impurity was also observed. Unfortunately, this small amount of impurity could only be removed through

(12) Sturla, S. J.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1976.
(13) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 6785.
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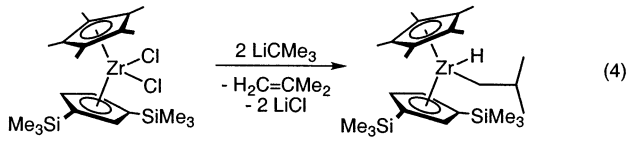
(25) (a) Zhou, R.; Wang, C.; Hu, Y.; Flood, T. C. *Organometallics* **1997**, *16*, 434. (b) Northcutt, T. O.; Wick, D. D.; Vetter, A. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 7257.
(26) Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7823.
(27) Pool, J. A.; Bradley, C. A.; Chirik, P. J. *Organometallics* **2002**, *21*, 1271.

successive recrystallizations, resulting in an overall 15% isolated yield for pure **2**.

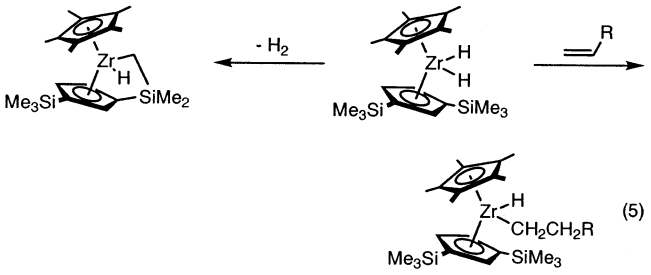
The zirconocene isobutyl hydride complex Cp*Cp″Zr-(CH_2CHMe_2)H (**6**) was also prepared by reaction of the zirconocene dichloride with 2 equiv of *tert*-butyllithium as described previously (eq 4).[27]



(4)

6

The zirconocene alkyl hydrides containing β-hydrogens (**3**−**6**) may also be prepared by olefin insertion into the zirconocene dihydride Cp*Cp″ZrH_2. Although this route provided the desired compounds, the alkyl hydride products are invariably contaminated with the zirconocene cyclometalated hydride (eq 5). For this reason the salt metathesis route is preferred. Attempts to prepare zirconocene alkyl hydrides with secondary alkyl ligands by reaction of **1** with cyclopentyl or cyclohexyllithium were unsuccessful. Likewise, attempts to insert cyclopentene or cyclohexene into Cp*Cp″ZrH_2 did not yield the desired alkyl hydride product.



(5)

Using the procedures described above, Cp*Cp″Zr(CH_2-$SiMe_3$)H (**8**), Cp*Cp″Zr(Ph)H (**9**), and Cp*Cp″Zr(CH_2-Ph)H (**10**) were also prepared and isolated as air- and moisture-sensitive solids in moderate yields (∼75%) by recrystallization from pentane (eq 3).

Each of the zirconocene alkyl hydride complexes, **2**−**10**, was readily identified by ^{1}H and ^{13}C NMR spectroscopy. Typical spectra display inequivalent [$SiMe_3$] groups, one Cp* resonance, and three cyclopentadienyl resonances on the Cp″ ring, consistent with C_1 molecular symmetry. Diagnostic Zr-*H* resonances are typically observed around 5 ppm in the ^{1}H NMR spectrum in benzene-d_6, although for **3** and **4**, relatively upfield values of 3.84 and 3.86 ppm are observed, respectively. The alkyl hydride complexes also display diastereotopic Zr-CH_2 hydrogens that are upfield of $SiMe_4$, consistent with a methylene unit coordinated to a chiral zirconium center.

Cooling a concentrated pentane solution of **2** to −35 °C produced clear, colorless crystals suitable for X-ray diffraction. The asymmetric unit contains two enantiomeric molecules, one of which is shown in Figure 1. The solid state structure reveals the expected coordination environment for a monomeric, bent metallocene. The X-ray data were of sufficient quality such that all of the hydrogen atoms, including the zirconium hydride, could be located and refined. The Zr−H distance of 1.85(3) Å and the Zr−C(1) distance of 2.282(2) Å are in accord

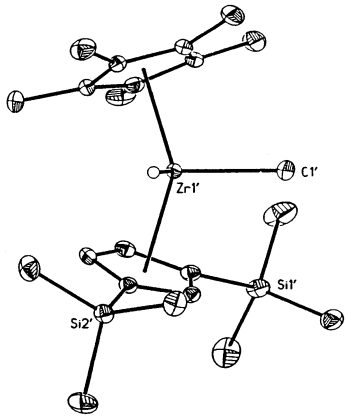
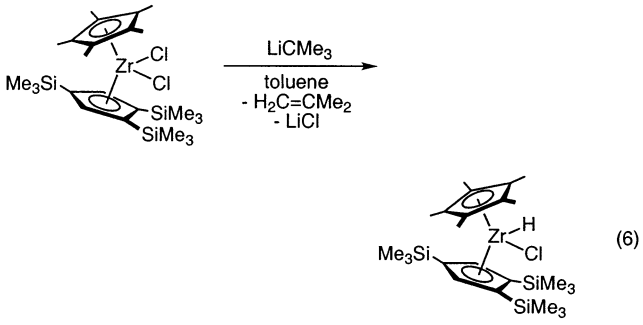


Figure 1. Molecular structure of one enantiomer of **2** with 30% probability ellipsoids. Hydrogen atoms, except the metal hydride, are omitted for clarity.

with those previously reported for zirconocene hydrides[27,28] and alkyls,[29] respectively.

A similar protocol produced X-ray quality crystals of the zirconocene benzyl hydride, **10**, and the molecular structure is shown in Figure 2. As with **2**, the X-ray data were of sufficient quality to locate each of the hydrogens in the molecule, providing a zirconium hydride distance of 1.81(2) Å. The most notable feature of the structure is the η^2 coordination of the benzyl ligand with a short Zr−C(12) distance of 2.7805(18) Å. This value is in agreement with the average distance of 2.618 Å found for zirconium η^2 benzyl complexes.[30]

In addition to studies with the [Cp*Cp″Zr] series, we also investigated the effect of alkyl substituents on the rate of reductive elimination with the more sterically hindered [Cp*Cp‴Zr] (Cp‴ = η^5-C_5H_2-1,2,4-($SiMe_3$)$_3$) motif. Preparation of the requisite hydrido chloride complex, Cp*Cp‴Zr(H)Cl (**11**), was accomplished by addition of 1 equiv of $LiCMe_3$ to a toluene solution of the zirconocene dichloride (eq 6).



(6)

11

Alkylation of **11** with $LiCH_3$ resulted in elimination of lithium chloride accompanied by clean formation of the zirconocene methyl hydride complex Cp*Cp‴Zr-(CH_3)H (**12**) (eq 7). Unlike **2**, pure **12** has been obtained

(28) (a) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 821. (b) Stones, S. B.; Peterson, J. L. *Inorg. Chem.* **1981**, *20*, 2889. (c) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973.

(29) (a) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 637. (b) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897. (c) Jordan, G. T.; Liu, F.-C.; Shore, S. G. *Inorg. Chem.* **1997**, *36*, 5597. (d) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293.

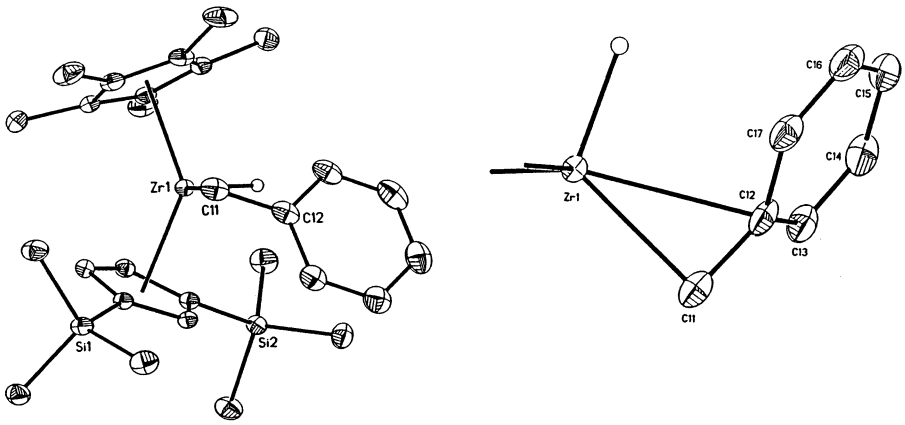
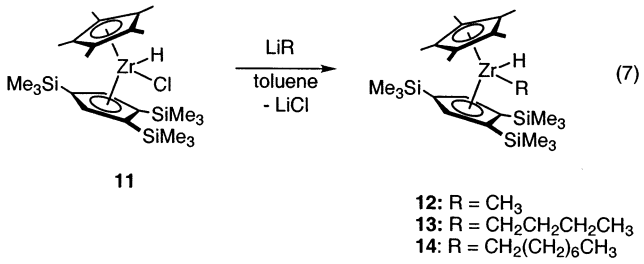


Figure 2. Molecular structure of **10** with 30% probability ellipsoids. Hydrogen atoms, except the metal hydride, are omitted for clarity.

directly from the reaction mixture without the need for successive recrystallizations. This methodology has also been extended to include the butyl hydride derivative Cp*Cp‴Zr($CH_2(CH_2)_2CH_3$)H (**13**) and the *n*-octyl hydride Cp*Cp‴Zr($CH_2(CH_2)_6CH_3$)H (**14**), both of which may be isolated as thick yellow oils in high yield (eq 7).

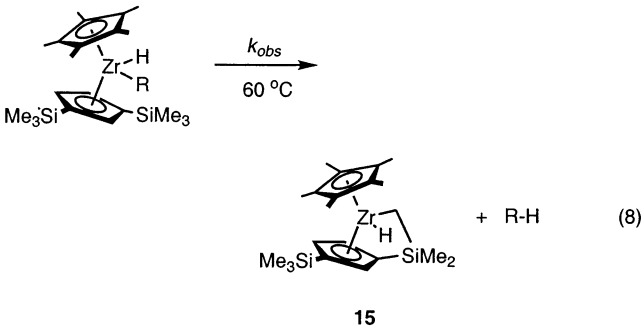


(7)

11

12: R = CH_3
13: R = $CH_2CH_2CH_2CH_3$
14: R = $CH_2(CH_2)_6CH_3$

Kinetics of Reductive Elimination. Thermolysis of the zirconocene alkyl hydrides Cp*Cp″Zr(R)H results in smooth, first-order elimination of alkane and cyclometalation of one of the cyclopentadienyl trimethylsilyl groups. As reported previously,[21] only one diastereomer of the cyclometalated zirconocene hydride, **15**, is observed (eq 8). These reactions are best viewed as a



(8)

15

composite of alkane reductive elimination followed by oxidative addition of a C−H bond of a [$SiMe_3$] substituent. The first-order rate constants for overall reductive elimination[31] were conveniently measured by ^{1}H NMR spectroscopy at 60 °C and were determined by integrating the resonances of the zirconocene alkyl hydride versus **15** as a function of time. The observed rate constants for reductive elimination for the zirconocene complexes **2**−**7** where the alkyl ligand was systematically varied are contained in Table 1.

Table 1. Rate Constants for Alkane Reductive Elimination for 2−7 at 60 °C

compound	R	k_{obs} (s^{-1})	k_{rel}
2	CH_3	$5.1(3) \times 10^{-6}$	1
3	$CH_2CH_2CH_2CH_3$	$4.9(3) \times 10^{-4}$	96
4	$CH_2(CH_2)_6CH_3$	$4.4(3) \times 10^{-4}$	86
5	$CH_2{}^cC_6H_{11}$	$4.4(1) \times 10^{-4}$	86
6	CH_2CHMe_2	$1.7(4) \times 10^{-3}$	333
7	CH_2CMe_3	$2.0(1) \times 10^{-3}$	392

Table 2. Rates of Reductive Elimination for 8−10 at 60 °C

compound	R	k_{obs} (s^{-1})
8	CH_2SiMe_3	$3.3(1) \times 10^{-6}$
9	Ph	$5.5(2) \times 10^{-6}$
10	CH_2Ph	$4.7(1) \times 10^{-5}$

In general, the rate of alkane formation increases as the steric disposition of the alkyl increases. This trend is in accord with data previously reported for late transition metal reductive elimination reactions.[22−24] The thermolysis of the zirconocene alkyl hydrides, **8**−**10**, was also studied. The measured first-order rate constants for reductive elimination for these complexes are contained in Table 2.

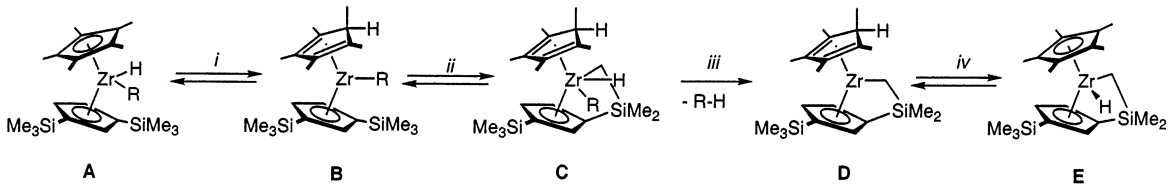
The rates of reductive elimination were also measured for the Cp*Cp‴Zr(R)H complexes at 60 °C (eq 9). As with the Cp*Cp″Zr(R)H reductive eliminations, one diastereomer of the cyclometaled hydride **16** is formed.[21,32] In this case, rate constants for the least sterically hindered complexes were measured because, at this temperature, the other reactions were too fast

(30) Cambridge Structural Database version 5.23. For representative examples of zirconium η^2-benzyl complexes: (a) Ziniuk, Z.; Goldberg, I.; Kol, M. *Inorg. Chem. Commun.* **1999**, *2*, 549. (b) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282. (c) Male, N. A. H.; Thorton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487. (d) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343.

(31) We use the term overall reductive elimination to signify the conversion of the zirconocene alkyl hydride to the corresponding cyclometalated hydride with loss of alkane. The observed rate constants, which we refer to as "rate constants for reductive elimination", are actually the products of several elementary steps (see Scheme 1).

(32) For other examples of [$SiMe_3$] group participation in low-valent zirconium chemistry see: (a) Horacek M.; Stepnicka P.; Kubista J.; Fejfarova K.; Gyepes R.; Mach K. *Organometallics* **2003**, *22*, 861. (b) Larsonneur, A.-M.; Choukroun, R.; Jaud, J. *Organometallics* **1993**, *12*, 3216.

Scheme 1

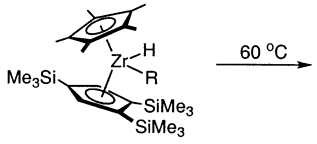


R = alkyl group

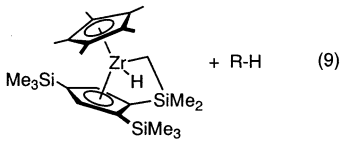
Table 3. Relative Rates of Alkane Reductive Elimination for 12−14 at 60 °C

compound	R	k_{obs} (s^{-1})	k_{rel}
12	CH_3	$1.0(2) \times 10^{-5}$	1
13	$CH_2CH_2CH_2CH_3$	$5.5(2) \times 10^{-3}$	550
14	$CH_2(CH_2)_6CH_3$	$1.0(5) \times 10^{-2}$	1000

to be accurately determined by ^1H NMR spectroscopy. The rate constants for reductive elimination for Cp*-Cp‴Zr(R)H complexes **12**, **13**, and **14** are contained in Table 3.



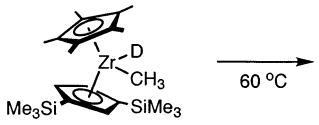
12: R = CH_3
13: R = $CH_2(CH_2)_2CH_3$
14: R = $CH_2(CH_2)_6CH_3$



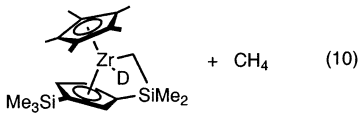
16

Isotopic Labeling Studies. Previous studies from our laboratory have focused on the mechanism of alkane reductive elimination from zirconocene isobutyl hydride complexes.[21] Isotopic labeling and kinetic isotope effects are consistent with a mechanism involving rapid migration of the zirconium hydride to the Cp* ring followed by rate-determining oxidative addition of a [$SiMe_3$] group. Reductive elimination of the alkane and subsequent hydrogen migration produce the observed zirconocene cyclometalated hydride. Isotopic labeling studies were conducted with isotopomers of **2** in order to determine whether this proposed mechanistic pathway was operable for alkyls other than isobutyl.

Preparation of Cp*Cp″Zr(D)Cl (**1-*d*$_1$**) was accomplished by addition of 1 equiv of $LiC(CD_3)_3$ to Cp*Cp″-$ZrCl_2$ as described previously.[27] Alkylation of **1-*d*$_1$** with $LiCH_3$ afforded Cp*Cp″Zr(CH_3)D (**2-*d*$_1$**). Thermolysis of **2-*d*$_1$** at 60 °C resulted in formation of CH_4 and the cyclometalated zirconocene deuteride **15-*d*$_1$** (eq 10). Analysis of the reaction mixture by a combination of ^1H and $^2H\{^1H\}$ NMR spectroscopy demonstrated that CH_4 was the only methane isotopomer produced and the deuterium atom remained in the organometallic product. Therefore, alkyls other than isobutyl seem to reductively eliminate by the pathway shown in Scheme 1.

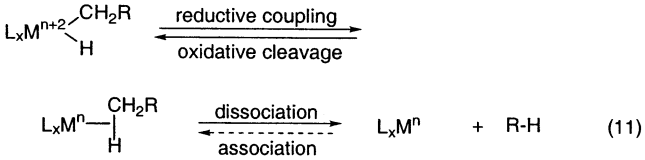


2-*d*$_1$

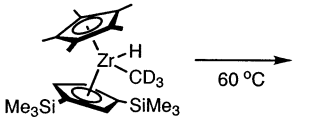


15-*d*$_1$

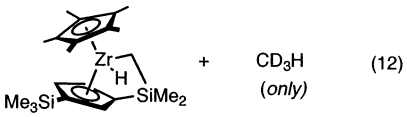
One open question regarding the mechanism proposed in Scheme 1 is the possibility of a reversible reductive elimination (step *iii*) and the intermediacy of an alkane σ-complex. Both Jones[33] and Parkin[17] have noted that what is commonly referred to as a "reductive elimination reaction" is actually a composite of two reactions, namely, reductive coupling of the alkyl and hydride ligands, followed by dissociation (eq 11). An intermediate alkane σ-complex or reassociation of the alkane with the zirconocene alkyl intermediate **D** (Scheme 1) would lead to multiple H/D exchange processes with an appropriately isotopically labeled alkyl hydride complex.



To probe this issue, Cp*Cp″Zr(CD_3)H (**2-*d*$_3$**) was prepared by addition of $LiCD_3$ to **1**. Thermolysis of **2-*d*$_3$** at 60 °C resulted in smooth formation of the zirconocene cyclometalated hydride **15** along with CD_3H as the sole methane isotopomer (eq 12). The absence of CD_2H_2 and

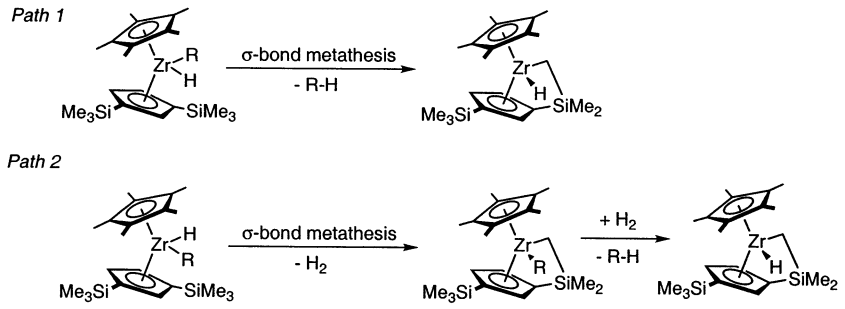


2-*d*$_3$



(33) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140.

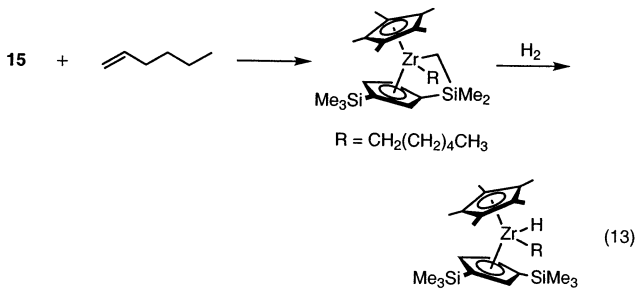
Scheme 2



other methane isotopomers demonstrates the irreversibility of the reductive elimination step; oxidative addition of free alkane is not competitive with hydrogen migration from the cyclopentadienyl ring to the metal center. Sole formation of CD_3H also demonstrates that the lifetimes of methane σ-complexes are not significant on the reductive elimination pathway.

Possibility of σ-Bond Metathesis. The kinetic and mechanistic data presented herein and in our previous report[21] do not definitively exclude σ-bond metathesis pathways (Scheme 2). One possibility is a concerted addition of a C−H bond from a [$SiMe_3$] group to the zirconium alkyl group, liberating alkane and forming the cyclometalated zirconocene hydride (path 1, Scheme 2). Although our isotopic labeling studies are consistent with this pathway, the preference for C−H bond activation of the alkyl group over the hydride is inconsistent with previous observations in related scandocene alkyls.[34]

Another possibility is concerted addition of the [$SiMe_3$] C−H bond to the zirconium hydride, liberating free dihydrogen and forming an unobserved cyclometalated zirconocene alkyl. To account for the observed products, the alkyl group must undergo selective hydrogenolysis to yield the cyclometalated zirconocene hydride (path 2, Scheme 2). The possibility of this pathway has been definitively excluded by hydrogenolysis of the cyclometalated zirconocene hexyl complex. Addition of dihydrogen results in initial formation of the zirconocene hexyl hydride rather than **15** and free hexane (eq 13). Over time, hydrogenation of the alkyl hydride is observed, affording the zirconocene dihydride Cp*Cp″ZrH_2[27] and hexane. On the basis of this result and observations contrary to those reported previously,[34] we do not favor σ-bond metathesis over the mechanism proposed in Scheme 1.



(13)

Explanation of the Observed Alkyl Effects on Reductive Elimination. As demonstrated by the rate constants in Table 1, the rate of reductive elimination of alkane increases modestly with the increased steric disposition of the alkyl ligand. For example, the neopentyl hydride complex **7** undergoes reductive elimination almost 400 times faster than the corresponding methyl hydride **2**. Provided that the mechanism proposed in Scheme 1 is operative, the observed alkyl effects may be rationalized on the basis of ground state effects. We previously have shown that competitive reductive elimination between Cp*Cp″$Zr(CH_2CHMe_2)H$ and Cp*(η^5-C_5H_3-1,3-$(Si(CD_3)_3)_2Zr(CH_2CHMe_2)H$ yields a primary kinetic isotope effect of 3.6(3) at 60 °C.[21] This result was interpreted as [$SiMe_3$] group oxidative addition as the rate-determining step during the alkane reductive elimination reaction.

On the basis of the proposed mechanism in Scheme 1, dominant transition state effects would yield *slower* rates of alkane loss as the size of the alkyl ligand increases. The larger alkyls would serve to hinder oxidative addition of the [$SiMe_3$] carbon−hydrogen bond and raise the overall activation barrier for reductive elimination. If ground state effects were dominant, an increased rate of reductive elimination with increased alkyl sterics would be anticipated. Unfavorable steric interactions between the bulky alkyl ligands and the cyclopentadienyl substituents would destabilize the ground state for the more hindered alkyl complexes and would result in a lower activation barrier for reductive elimination. The observed kinetic data clearly support ground state destabilization as the dominant effect for the increased rates of reductive elimination.

To further substantiate our hypothesis, similar studies were also conducted with a more substituted cyclopentadienyl ligand. A more voluminous ligand array would be expected to magnify the observed ground state effects and increase the overall rate of reductive elimination as well as provide greater kinetic discrimination between similar alkyl ligands (e.g., $CH_2(CH_2)_2CH_3$ versus $CH_2(CH_2)_6CH_3$). Comparison of the rate constants in Table 2 for the Cp*Cp″Zr(R)H series to those in Table 3 for the Cp*Cp‴Zr(R)H complexes supports this hypothesis. Comparing the methyl derivatives **2** and **12** reveals a doubling in rate constant for reductive elimination upon addition of a [$SiMe_3$] to one cyclopentadienyl ring. The difference in rate constants increases with the size of the alkyl ligand. For example, the *n*-butyl derivatives **3** and **13** display an 11-fold rate enhancement upon addition of a [$SiMe_3$] group, whereas the more bulky *n*-octyl complexes **4** and **14** offer a 22-fold rate enhancement.

The more sterically hindered cyclopentadienyl ligand environment also magnifies subtle differences between

(34) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

similar alkyl ligands. For the [Cp*Cp″Zr] ligand motif, the rate constants for reductive elimination between the *n*-butyl derivative **3** and the *n*-octyl complex **8** are indistinguishable within experimental error. However, for the [Cp*Cp‴Zr] series, the *n*-octyl derivative **14** reductively eliminates alkane approximately twice as fast as the *n*-butyl complex **13**. More substantial effects are observed in changing the alkyl from methyl to a long chain hydrocarbon. In the [Cp*Cp″Zr] case, the methyl reductively eliminates approximately 100 times slower than the *n*-butyl, whereas addition of a cyclopentadienyl [$SiMe_3$] group results in a 550-fold rate enhancement. All of the observations are consistent with ground state destabilization being the most important factor governing the rate of alkane reductive elimination.

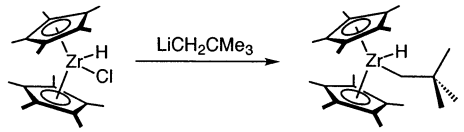
The ground state effect is also manifested, perhaps more subtly, with other types of alkyl ligands. For example, the trimethylsilylmethyl hydride **8** undergoes reductive elimination *slower* than the corresponding neopentyl hydride **7**. At first glance this observation may seem inconsistent with the proposed ground state destabilization model. However, the longer carbon−silicon bond length in $ZrCH_2-SiMe_3$ as compared to $ZrCH_2-CMe_3$ removes unfavorable steric interactions with the cyclopentadienyl substituents. This assertion is supported by the average carbon−silicon bond length of 2.187(95) Å versus carbon−carbon bond lengths of 1.534(16) Å reported for group 4 transition metal alkyls of this type.[35] Similar explanations have been proposed for the difference in the rate of α-elimination in the decomposition of the homoleptic tantalum alkyls, $Ta(CH_2ESiMe_3)_5$ (E = Si > C),[36] as well as in thermal alkane eliminations from silica-supported chromium alkyls.[37]

Ground state effects may also be used to explain the relatively slow rates of reductive elimination of the phenyl and benzyl hydrides **9** and **10**. For the latter, η^2 coordination of the benzyl ligand provides electronic saturation at the metal center and hence stabilizes the ground state and slows the rate of reductive elimination. The phenyl hydride **9** reductively eliminates alkane at a rate comparable to the methyl hydride **2**. Although the planarity of the phenyl ring may be in part responsible for the slow loss of benzene, the relatively high metal−carbon bond strength is the more likely explanation. Bergman has rationalized the slower reductive elimination of benzene as compared to cyclohexane in Cp*Ir(PMe_3)(R)H complexes on the basis of the increased iridium bond enthalpy for the phenyl complex.[38] Jones and Feher also estimated a 13 kcal/mol *increase* in the bond enthalpy for rhodium−phenyl versus rhodium−methyl complexes.[39] A similar rationale was also used to explain relatively slow rates of benzene reductive elimination in tantalocene phenyl dihydride complexes.[40] Studies by Wolczanski[41] have also noted the increased strength of the titanium−phenyl bond relative to other alkyl substituents.

Application of Alkyl Substituent Effects to Dinitrogen Activation. We have previously demonstrated that manipulation of cyclopentadienyl ring substituents may be used to increase the rate of alkane reductive elimination to form cyclometalated zirconocene hydrides that are reactive toward atmospheric nitrogen.[21] It is important to note that it is the stability of the cyclometalated hydride, not the alkyl hydride, that dictates reactivity toward dinitrogen. We therefore hypothesized that alkyl effects may be used to increase the rate of reductive elimination in a zirconocene complex that forms a N_2-reactive cyclometalated hydride.

As a demonstration of principle, we focused on the reductive elimination of $Cp^*_2Zr(R)H$ complexes. This ligand set was chosen because the dinitrogen complex $[Cp^*_2Zr(\eta^1\text{-}N_2)]_2(\mu_2\text{-}N_2)$ (**18**) has been previously synthesized by sodium amalgam reduction of the corresponding dichloride complex.[42] Presumably alkali metal reduction affords a zirconocene cyclometalated hydride which upon exposure to N_2 forms **18**. It should also be noted that $Cp^*_2Zr(CH_2CHMe_2)H$ has been prepared and its thermal reductive elimination studied.[14] However, the temperatures required to initiate isobutane reductive elimination from the isobutyl hydride exceed the thermal stability of **18**, thus precluding isolation of the N_2 complex by reductive elimination. Preparation of sterically demanding alkyl hydride complexes may take advantage of the ground state destabilization phenomenon and hence lower the activation barrier for alkane loss and provide a facile route to **18** under the relatively mild and reproducible conditions of reductive elimination.

Synthesis of $Cp^*_2Zr(H)Cl$ (**16**) has been achieved by addition of 1 equiv of $LiCMe_3$ to the corresponding dichloride complex as described previously.[21] Alkylation with 1 equiv of $LiCH_2CMe_3$ in toluene affords $Cp^*_2Zr(CH_2CMe_3)H$ (**17**) as a yellow crystalline solid in 69% yield (eq 14). The ^1H NMR spectrum of **17** in benzene-d_6 displays a Cp* resonance at 1.94 ppm, alkyl resonances at 0.06 (CH_2) and 1.22 (CMe_3), and a zirconium hydride resonance at 6.59 ppm in accord with previously reported alkyl hydride complexes.[14,21,27]

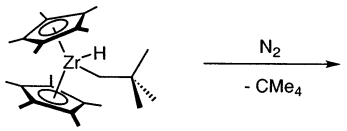


16 **17** (14)

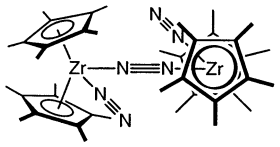
Stirring a toluene solution of **17** at 22 °C under 1 atm of pure dinitrogen over the course of 2 weeks resulted in slow reductive elimination of neopentane and formation of the dinitrogen complex **18** (eq 15) in 75% yield. In addition to **18**, small, variable amounts (10−20%) of the dihydride complex $Cp^*_2ZrH_2$ were also observed. We believe the dihydride complex arises from stirring **18** for extended periods, resulting in decomposition by cyclometalation with liberation of free H_2.[43] Attempts

(35) Cambridge Structural Database version 5.23.
(36) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746.
(37) Ajou, J. A. N.; Rice, G. L.; Scott, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 13436.
(38) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.
(39) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.
(40) Bregel, D. C.; Oldham, S. M.; Eisenberg, R. *J. Am. Chem. Soc.* **2002**, *124*, 13827.
(41) Bennett, J. L.; Vaid, T. P.; Wolczanski, P. T. *Inorg. Chim. Acta* **1998**, *270*, 414.
(42) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229.
(43) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973.

to increase the rate of reductive elimination and hence dinitrogen complex formation by incorporation of bulky methyladamantyl ligands produced only modest rate enhancements.



17



18 (15)

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high-vacuum line, Schlenk, or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[44] In addition, toluene and pentane were further dried by storage over titanocene[45] and were vacuum transferred immediately before use. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over titanocene. Argon and hydrogen gas were purchased from Airgas Incorporated and passed through a column containing Ridox oxygen scavenger and 4 Å molecular sieves before admission to the high-vacuum line. Preparations of **1**,[27] **7**,[27] Cp*Cp‴$ZrCl_2$,[21] **15**,[21] and **16**[21] were accomplished using procedures described previously.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD area detector system equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Preparation of Cp*Cp″Zr(CH_3)H (2). A scintillation vial was charged with 211 mg (0.447 mmol) of **1** and approximately 10 mL of toluene. The solution was chilled in the cold well, and 279 μL of 1.6 M MeLi in diethyl ether was added. The resulting reaction mixture was warmed to room temperature and stirred for 10 h, after which time the white precipitate was removed by filtration through Celite. The solvent was then removed in vacuo, leaving a powder blue oil. Repeated recrystallization from pentane afforded 32 mg (16%) of analytically pure colorless crystals. Anal. Calcd for $C_{22}H_{40}Si_2Zr$: C, 58.47; H, 8.92. Found: C, 58.25; H, 9.23. ^{1}H NMR (benzene-d_6): δ −0.34 (s, 3H, Zr-CH_3), 0.21 (s, 9H, SiMe_3), 0.37 (s, 9H, SiMe_3), 1.89 (s, 15H, C_5Me_5), 5.15 (m, 1H, Cp), 5.37 (m, 1H, Cp), 6.75 (m, 1H, Cp), 5.75 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 0.72, 0.79 (SiMe_3), 12.52 (C_5Me_5), 44.17 (Zr-CH_3), 115.58, 116.94, 123.58, 125.58, 126.57 (Cp), 117.93 (C_5Me_5).

Preparation of Cp*Cp″Zr($CH_2(CH_2)_2CH_3$)H (3). A scintillation vial was charged with 55 mg (0.12 mmol) of Cp*Cp″Zr(H)Cl and approximately 10 mL of pentane. The solution was chilled in the cold well, and 73 μL (0.12 mmol) of 1.6 M ^{n}BuLi in hexane was added. The resulting reaction mixture was warmed to room temperature and stirred for 15 min, after which time the white precipitate was removed by filtration through Celite. The solvent was then removed in vacuo, leaving 45 mg (76%) of a yellow oil identified as **3**. ^{1}H NMR (benzene-d_6): δ −0.39 (m, 2H, CH_2CH$_2$CH$_2$CH$_3$), 0.27 (s, 9H, SiMe_3), 0.41 (s, 9H, SiMe_3), 1.09 (t, 3H, CH$_2$CH$_2$CH$_2$CH_3), 1.30 (m, 4H, CH$_2$CH_2CH$_2$CH$_3$), 1.82 (s, 15H, C_5Me_5), 3.84 (s, 1H, Zr-*H*), 5.16 (m, 1H, Cp), 5.29 (m, 1H, Cp), 5.51 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ 0.89 (SiMe$_3$), 0.93 (SiMe$_3$), 12.09, 14.81, 28.50, 37.43 (CH$_2$CH$_2$CH$_2$CH$_3$), 12.40 (C_5Me_5), 112.81, 113.99, 114.70, 121.01, 123.04, 125.64 (Cp), 119.49 (C_5Me$_5$).

Preparation of Cp*Cp″Zr($CH_2(CH_2)_6CH_3$)H (4). This compound was prepared in a manner identical to **3** employing 84 mg (0.15 mmol) of **1** and 19 mg (0.15 mmol) of LiCH$_2$(CH$_2$)$_6$CH$_3$, yielding 77 mg (74%) of a yellow oil identified as **4**. ^{1}H NMR (benzene-d_6): δ −0.002 (m, 2H, CH_2(CH$_2$)$_6$CH$_3$), 0.29 (s, 9H, SiMe_3) 0.43 (s, 9H, SiMe_3), 0.92 (t, 3H, CH$_2$(CH$_2$)$_6$CH_3), 1.24−1.40 (m, 12H, CH$_2$(CH_2)$_6$CH$_3$), 1.84 (s, 15H, C_5Me_5), 3.86 (s, 1H, Zr-*H*), 5.17 (m, 1H, Cp), 5.30 (m, 1H, Cp), 5.56 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ 0.92, 0.96 (SiMe$_3$), 12.42 (C_5Me_5), 29.85, 30.58, 32.32, 32.38, 35.56, 37.76, 37.99 (CH$_2$(CH$_2$)$_6$CH$_3$), 65.89 (CH$_2$(CH$_2$)$_6$CH$_3$)112.79, 113.99, 116.76, 119.51, 123.05 (Cp), 114.69 (C_5Me$_5$).

Preparation of Cp*Cp″Zr($CH_2{}^cC_6H_{11}$)H (5). This compound was prepared in a manner identical to **3** employing 96 mg (0.20 mmol) of **1** and 21 mg (0.20 mmol) of LiCH$_2$(CH$_2$)$_6$CH$_3$, yielding 96 mg (86%) of a yellow oil identified as **5**. ^{1}H NMR (benzene-d_6): δ −0.36 (m, 1H, C$H_2{}^cC_6$H$_{11}$), −0.34 (m, 1H, C$H_2{}^cC_6$H$_{11}$), 0.24 (s, 9H, SiMe$_3$), 0.29 (s, 9H, SiMe$_3$), 0.87, 1.19, 1.44, 1.72 (m, H, CH$_2{}^cC_6H_{11}$), 1.89 (s, 15H, C_5Me_5), 5.07 (m, 1H, Cp), 5.36 (m, 1H, Cp), 5.75 (s, 1H, Zr-*H*), 6.79 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ 1.11 (SiMe$_3$), 12.86 (C_5Me_5), 27.07, 27.36, 27.72, 27.88, 34.04, 40.34, 41.41 (CH$_2{}^cC_6$H$_{11}$), 68.40 (C$H_2{}^cC_6$H$_{11}$), 115.86, 117.78, 117.97, 123.57, 129.52 (Cp), 123.96 (C_5Me$_5$).

Preparation of Cp*Cp″Zr(CH_2CMe_3)H (7). A scintillation vial was charged with 88 mg (0.19 mmol) of Cp*Cp″Zr(H)Cl and about 10 mL of pentane. The solution was chilled in the cold well, and 15 mg (0.19 mmol) of LiCH$_2$Me$_3$ was dissolved in pentane and added to the solution. The resulting reaction mixture was warmed to room temperature and stirred for 1 h, after which time the white precipitate was removed by filtration through Celite. The solvent was then removed in vacuo, leaving 63 mg (67%) of a yellow oil identified as **7**. ^{1}H NMR (benzene-d_6): δ 0.24 (s, 9H, SiMe$_3$), 0.37 (s, 9H, SiMe$_3$), 1.19 (s, CH$_2$CMe_3), 1.89 (s, 15H, C_5Me_5), 4.96 (m, 1H, Cp), 5.46 (m, 1H, Cp), 7.30 (m, 1H, Cp), 6.15 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 0.88 (SiMe$_3$), 1.18 (SiMe$_3$), 12.88 (C_5Me_5), 37.03 (CH$_2$CMe_3), 39.17 (CH$_2$CMe$_3$), 69.40 (CH_2CMe$_3$), 116.28, 117.43, 123.11, 123.27, 129.68 (Cp), 118.48 (C_5Me$_5$).

Preparation of Cp*Cp″Zr(CH_2SiMe_3)H (8). This compound was prepared in a manner identical to **3** employing 57 mg (0.12 mmol) of **1** and 11 mg (0.12 mmol) of LiCH$_2$SiMe$_3$ and diethyl ether as a solvent. This procedure yielded 47 mg (75%) of a yellow oil identified as **8**. ^{1}H NMR (benzene-d_6): δ −0.57 (d, 1H, CH_2SiMe$_3$), −0.22 (d, 1H, CH_2SiMe$_3$), 0.21 (s, 9H, SiMe_3), 0.26 (s, 9H, SiMe_3), 0.36, (s, 9H, SiMe_3), 1.88 (s, 15H, C_5Me_5), 5.01 (m, 1H, Cp), 5.48 (m, 1H, Cp), 6.96 (m, 1H, Cp), 5.87 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 0.71 (SiMe_3), 1.28 (SiMe_3), 5.50 (SiMe_3), 12.80 (C_5Me_5), 49.38 (CH_2SiMe$_3$), 115.95, 117.37, 122.25, 123.24, 129.33 (Cp), 118.14 (C_5Me$_5$).

Preparation of Cp*Cp″Zr(Ph)H (9). This compound was prepared in a manner identical to **3** employing 91 mg (0.21 mmol) of **1** and 420 μL of 0.5 M (0.21 mmol) PhLi, yielding 79

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mg (73%) of a white solid identified as **9**. ^{1}H NMR (benzene-d_6): δ 0.28, 0.45 (s, 18H, SiMe_3), 1.76 (s, 15H, C_5Me_5), 5.24 (m, 1H, Cp), 5.36 (m, 1H, Cp), 5.51 (m, 1H, Cp), 5.31 (s, 1H, Zr-*H*), 7.02 (d, 2H, o-C_6H_5), 7.09 (t, 2H, p-C_6H_5), 7.29 (d, 2H, m-C_6H_5). ^{13}C NMR (benzene-d_6): δ 0.25 (SiMe_3), 1.00 (SiMe_3), 12.06 (C_5Me_5), 115.94, 121.78, 122.95, 124.11, 126.62, 127.01, 136.76 (Cp, *Ph*), 117.02 (C_5Me$_5$).

Preparation of Cp*Cp″Zr(CH$_2$Ph)H (10). This compound was prepared in a manner identical to **3** employing 0.105 g (0.223 mmol) of **1** and 29 mg (0.223 mmol) of KCH$_2$Ph, yielding 96 mg (82%) of an orange solid identified as **10**. Anal. Calcd for $C_{28}H_{42}Si_2Zr$: C, 63.69; H, 8.02. Found: C, 63.78; H, 8.42. ^{1}H NMR (benzene-d_6): δ 0.21 (s, 9H, SiMe_3), 0.24 (s, 9H, SiMe_3), 1.24 (d, 1H, CH_2Ph), 1.77 (d, 1H, CH_2Ph), 1.86 (s, 15H, C_5Me_5), 5.00 (m, 1H, Cp), 5.35 (m, 1H, Cp), 6.17 (m, 1H, Cp), 5.55 (s, 1H, Zr-*H*), 6.78 (d, 2H, C_6H_5), 6.92 (t, 1H, *p*-C_6H_5), 7.20 (d, 2H, C_6H_5). ^{13}C NMR (benzene-d_6): δ 0.86 (SiMe_3), 1.27 (SiMe_3), 12.64 (C_5Me_5), 61.72 (*C*H$_2$Ph), 115.94, 121.56, 123.99, 124.68, 126.19, 126.24, 126.72, 128.44, 129.27 (Cp, CH$_2$*Ph*), 117.77 (C_5Me$_5$).

Preparation of Cp*Cp‴Zr(H)Cl (11). In the drybox, a 50 mL round-bottom flask was charged with 290 mg (0.502 mmol) of Cp*Cp‴ZrCl$_2$, which was then dissolved in approximately 20 mL of toluene. The solution was placed in the cold well until frozen. While thawing, 334 μL of 1.5 M ^{t}BuLi was added by microsyringe. The resulting reaction mixture was warmed to room temperature and stirred. After 2 h, a white precipitate formed and was removed by filtration through a pad of Celite. The solvent was removed in vacuo from the resulting solution, leaving a brown oil. Recrystallization from pentane afforded 172 mg (63%) of a light brown powder identified as **11**. Anal. Calcd for $C_{24}H_{45}Cl_1Si_3Zr_1$: C, 52.94; H, 8.33. Found: C, 52.45; H, 7.96. ^{1}H NMR (benzene-d_6): δ 0.26 (s, 9H, SiMe_3), 0.32 (s, 9H, SiMe_3), 0.51 (s, 9H, SiMe_3), 2.01 (s, 15H, C_5Me_5), 6.00, 6.91 (m, 2H, Cp), 6.89 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 1.28 (SiMe$_3$), 2.19 (SiMe$_3$), 2.40 (SiMe$_3$), 13.34 (C_5Me_5), 123.29, 124.73, 125.26, 131.26, 133.45, 136.99 (Cp), 121.17 (C_5Me$_5$).

Preparation of Cp*Cp‴Zr(CH$_3$)H (12). This compound was prepared in a manner identical to **3** employing 54 mg (0.099 mmol) of **11** and 62 μL (0.099 mmol) of 1.6 M MeLi, yielding 43 mg (83%) of a yellow oil identified as **12**. ^{1}H NMR (benzene-d_6): δ −0.30 (s, 3H, Zr-*C*H$_3$), 0.19 (s, 9H, SiMe$_3$), 0.32 (s, 9H, SiMe$_3$), 0.47 (s, 9H, SiMe$_3$), 2.00 (s, 15H, C_5Me_5), 5.69 (m, 1H, Cp), 7.18 (m, 1H, Cp), 6.12 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 1.22 (SiMe$_3$), 2.35 (SiMe$_3$), 2.40 (SiMe$_3$), 13.07 (C_5Me_5), 44.42 (*C*H$_3$), 114.93, 123.39, 125.47, 129.81, 135.61 (Cp), 118.84 (C_5Me$_5$).

Preparation of Cp*Cp‴Zr(CH$_2$CH$_2$CH$_2$CH$_3$)H (13). This compound was prepared in a manner identical to **3** employing 80 mg (0.150 mmol) of **11** and 92 μL (0.15 mmol) of 1.6 M ^{n}BuLi, yielding 53 mg (61%) of a yellow oil identified as **13**. ^{1}H NMR (benzene-d_6): δ −1.84 (m, 1H, CH_2CH$_2$CH$_2$CH$_3$), 0.25 (s, 9H, SiMe$_3$), 0.36 (s, 9H, SiMe$_3$), 0.49 (s, 9H, SiMe$_3$), 1.04 (t, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.42 (m, 3H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.99 (s, 15H, C_5Me_5), 5.54 (m, 1H, Cp), 7.24 (m, 1H, Cp), 5.62 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 1.47 (SiMe$_3$), 2.39 (SiMe$_3$), 2.52 (SiMe$_3$), 13.02 (C_5Me$_5$), 14.01, 25.15, 30.19, 34.49 (CH$_2$CH$_2$-CH$_2$CH$_3$), 114.93, 119.06, 119.45, 125.44, 132.92 (Cp), 118.14 (C_5Me$_5$).

Preparation of Cp*Cp‴Zr(H)^{n}Octyl (14). This compound was prepared in a manner identical to **3** employing 75 mg (0.140 mmol) of **11** and 19 mg (0.16 mmol) of LiCH$_2$(CH$_2$)$_6$-CH$_3$, yielding 42 mg (53%) of a yellow oil identified as **13**. ^{1}H NMR (benzene-d_6): δ −1.79 (m, 2H, CH_2(CH$_2$)$_6$CH$_3$), 0.26 (s, 9H, SiMe$_3$) 0.36 (s, 9H, SiMe$_3$), 0.50 (s, 9H, SiMe$_3$), 0.92 (t, 3H, CH$_2$(CH$_2$)$_6$C*H*$_3$), 1.23−1.52 (m, 12H, CH$_2$(C*H*$_2$)$_6$CH$_3$), 2.00 (s, 15H, C_5Me_5), 5.55 (m, 1H, Cp), 5.63 (s, 1H, Zr-*H*), 7.26 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ 1.47, 2.42, 2.53 (SiMe_3), 13.05 (C_5Me_5), 29.98, 30.12, 32.45, 32.33, 32.10, 37.51 (CH$_2$(*C*H)$_6$-CH$_3$), 71.91 (*C*H$_2$(CH)$_6$CH$_3$), 119.51, 119.44, 121.45, 125.45, 132.97 (Cp), 118.13 (C_5Me$_5$).

Preparation of Cp*$_2$ZrNpH (17). A scintillation vial was charged with 186 mg (0.47 mmol) of **16** and approximately 10 mL of toluene. The solution was chilled in the cold well, and 36 mg (0.47 mmol) of LiCH$_2$CMe$_3$ was dissolved in pentane and added to the solution. The resulting reaction mixture was warmed to room temperature and stirred for 10 h, after which time, the white precipitate was removed by filtration through Celite. The solvent was then removed in vacuo, leaving 139 mg of a yellow solid (69%) identified as **17**. Anal. Calcd for $C_{25}H_{42}Zr_1$: C, 69.21; H, 9.76. Found: C, 69.10; H, 9.43. ^{1}H NMR (benzene-d_6): δ 0.060 (s, 2H, *C*H$_2$CMe$_3$), 1.23 (s, 9H, CH$_2$C*Me*$_3$), 1.94 (s, 15H, C_5Me_5), 6.59 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 12.57 (C_5Me_5), 37.39 (CH$_2$C*Me*$_3$), 38.47 (CH$_2$-*C*Me$_3$), 68.32 (*C*H$_2$CMe$_3$), 118.40 (C_5Me$_5$).

Preparation of [Cp*$_2$ZrN$_2$]$_2$(μ-N$_2$) (18) by Reductive Elimination. A 25 mL round-bottom flask was charged with 0.068 g (0.157 mmol) of **17** and approximately 10 mL of pentane. The resulting reaction mixture was stirred for 2 weeks, after which time the solvent was removed in vacuo, leaving a purple solid. Recrystallization from pentane afforded 0.052 g (75%) of **18** by comparison to previously reported data.[42]

Reaction of 15 with 1-Hexene. A J. Young NMR tube was charged with 51 mg (0.12 mmol) of **15**, and approximately 0.5 mL of benzene-d_6 was added. On the vacuum line, 1 equiv of 1-hexene was added via calibrated gas bulb. The tube was shaken thoroughly. ^{1}H NMR (benzene-d_6): δ −3.00, −0.21 (d, 2H, ZrC*H*$_2$SiMe$_2$), −0.01 (dt, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 0.27 (s, 9H, SiMe$_3$), 0.64 (s, 3H, SiMe$_2$), 0.95 (t, 3H, C*H*$_2$CH$_2$-CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.39 (m, 8H, 1.67 (s, 15H, CpMe$_5$), 5.08, 5.20, 6.20 (m, 3H, Cp), 8.96 (s, 1H, *H*N$_3$SiMe$_3$) 1 SiMe$_2$ peak *not located*. ^{13}C NMR (benzene-d_6): δ −0.80, 2.97 (SiMe$_2$), 1.57 (SiMe$_3$), 12.71 (C_5Me_5), 13.51, 15.28, 24.05, 32.95, 36.47, 38.49 (hexyl) 55.79 (ZrC*H*$_2$SiMe$_2$), 114.30, 114.90, 116.45, 119.75, 125.12 (Cp), 117.72 (C_5Me$_5$).

General Procedure for Kinetic Determinations. In the drybox, 0.50 mL of a 0.070 M stock solution of the desired zirconocene alkyl hydride in benzene-d_6 was charged into a J. Young NMR tube and sealed with a Teflon valve. The NMR probe was calibrated to the desired temperature using an ethylene glycol standard, and the sample was inserted into the probe. Approximately 10−15 spectra were recorded at regular intervals over the duration of 2−3 half-lives. Peak intensities of the reactant and product were measured. The observed rate constants were obtained from slopes of plots of ln[Cp*(CpR$_n$)Zr(R′)H)] versus time.

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Supporting Information Available: Crystallographic data for **2** and **10** including full atom labeling schemes and bond distances and angles. Representative NMR spectra and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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