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Cyclopentadienyl Substituent Effects on Reductive Elimination Reactions in Group 4 Metallocenes: Kinetics, Mechanism, and Application to Dinitrogen Activation

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Abstract: The rate of reductive elimination for a family of zirconocene isobutyl hydride complexes, Cp*(CpR$_n$)Zr(CH$_2$CHMe$_2$)H (Cp* = η^5-C$_5$Me$_5$, CpR$_n$ = substituted cyclopentadienyl), has been measured as a function of cyclopentadienyl substituent. In general, the rate of reductive elimination increases modestly with the incorporation of sterically demanding substituents such as [CMe$_3$] or [SiMe$_3$]. A series of isotopic labeling experiments was used to elucidate the mechanism and rate-determining step for the reductive elimination process. From these studies, a new zirconocene isobutyl hydride complex, Cp″$_2$Zr(CH$_2$CHMe$_2$)(H) (Cp″ = η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$), was designed and synthesized such that facile reductive elimination of isobutane and activation of dinitrogen was observed. The resulting dinitrogen complex, [Cp″$_2$Zr]$_2$(μ_2, η^2,η^2-N$_2$), has been characterized by X-ray diffraction and displays a bond length of 1.47 Å for the N$_2$ ligand, the longest observed in any metallocene dinitrogen complex. Solution magnetic susceptibility demonstrates that [Cp″$_2$Zr]$_2$(μ_2, η^2, η^2-N$_2$) is a ground-state triplet, consistent with two Zr(III), d^1 centers. Mechanistic studies reveal that the dinitrogen complex is derived from the reaction of N$_2$ with the resulting cyclometalated zirconocene hydride rather than directly from reductive elimination of alkane.

Introduction

Group 4 metallocenes have attracted considerable attention due to their applications in olefin polymerization and other stoichiometric and catalytic reactions.[1] This rich chemistry is dominated by the M(IV), d^0 oxidation state, although low-valent titanocenes, zirconocenes, and hafnocenes also promote a variety of noteworthy transformations.[2] Interest in these molecules originates with Wilkinson's attempt to prepare the parent titanocene, [Cp$_2$Ti^{II}],[3,4] but has been expanded to include several examples, spanning all members of the triad. Diverse applications range from organic synthesis[5,6] to the activation of small molecules such as carbon monoxide[7] and dinitrogen.[8−11]

Synthesis of low-valent group 4 metallocenes is typically achieved by adding strong alkali metal reducing agents such as sodium amalgam to the corresponding metallocene dichloride, (R$_n$Cp)$_2$MCl$_2$. Despite numerous successes using this approach, these reactions are often unpredictable and subject to ill-defined substituent effects. These complications are particularly relevant to dinitrogen activation where Cp*$_2$ZrCl$_2$ (Cp* = η^5-C$_5$Me$_5$) undergoes facile reduction with 40% sodium amalgam to afford [Cp*$_2$Zr(η^1-N$_2$)]$_2$(μ_2, η^1, η^1-N$_2$),[12] but related zirconocenes such as Cp″$_2$ZrCl$_2$ and Cp$^{tt}_2$ZrCl$_2$ (Cp″ = η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$, Cp^{tt} = η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$) only undergo one-electron reduction to the Zr(III) monochloride under similar conditions.[13,14] In fact, Cp*$_2$ZrCl$_2$ is the only zirconocene known that forms a dinitrogen complex using alkali metal reducing agents. It should be noted, however, that titanocenes[15] and noncyclopentadienyl ligated zirconium complexes undergo smooth alkali metal (or equivalent) reduction to yield dinitrogen complexes.[8]

Reductive elimination of alkane (or dihydrogen) from a zirconocene alkyl hydride (or dihydride) represents an attractive, mild alternative for the synthesis of low-valent group 4 transition metal dinitrogen complexes. Although reductive elimination reactions are ubiquitous[16−23] and mechanistically well-estab-

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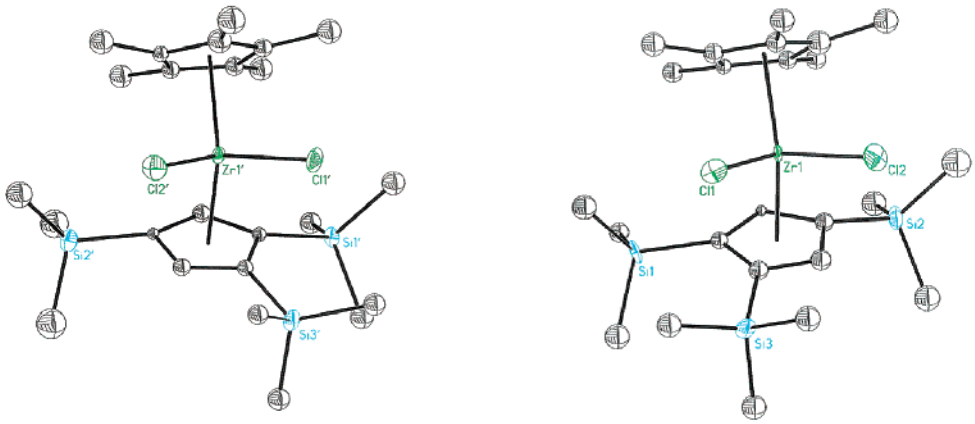


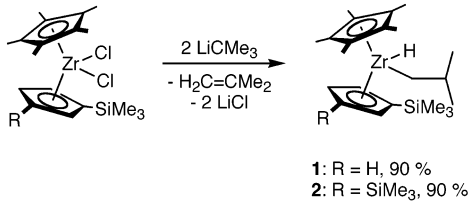
Figure 1. Molecular structure of Cp*(η^5-C_5H_2-1,2,4-$(SiMe_3)_3$)$ZrCl_2$ (**3-Cl$_2$**) at 50% probability ellipsoids.

lished[24−28] for d^6 and d^8 late transition metal complexes, reports of this transformation in group 4 transition metal chemistry are sparse. One pathway, referred to as a "ligand-induced" reductive elimination, involves addition of σ-donating ligands such as tertiary phosphines to $Cp_2Zr(R)H$ complexes, liberating alkane and forming the Zr(II)-ligand adduct, for example, $Cp_2Zr(PR_3)_2$.[29]

Reductive elimination reactions that occur thermally, without addition of exogenous ligands, have also been observed. Thermolysis of $Cp^*_2Zr(CH_2CHMe_2)H$ at 74 °C results in smooth, first-order elimination of isobutane along with a variety of zirconocene products.[30] Other examples of reductive elimination reactions involving group 4 transition metals have also been reported.[31−35] Despite these observations, a detailed understanding of the ancillary ligand effects on this fundamental organometallic reaction has not been disclosed. In this article, we describe the first systematic study of reductive elimination in early transition metal chemistry and apply the conclusions from these studies to the synthesis of a side-on bound, paramagnetic zirconocene dinitrogen complex. Relative rates of reductive elimination as a function of cyclopentadienyl substitution, mechanistic details, and the scope of the reductive elimination process as it applies to dinitrogen activation are described.

Results and Discussion

Synthesis of Zirconocene Alkyl Hydride Complexes. We began our investigations of early transition metal reductive elimination reactions with a family of zirconocene isobutyl hydride complexes. We recently discovered a convenient method for their preparation,[36] illustrated by the efficient synthesis of $Cp^*Cp'Zr(CH_2CHMe_2)H$ (Cp′ = η^5-C_5H_4-$SiMe_3$, **1**) and $Cp^*Cp''Zr(CH_2CHMe_2)H$ (**2**) which were isolated as yellow oils (eq 1).



This study also included the highly silylated zirconocene isobutyl hydride, $Cp^*Cp'''Zr(CH_2CHMe_2)H$ (**3**, Cp‴ = η^5-C_5H_2-1,2,4-$(SiMe_3)_3$). Preparation of the requisite zirconocene dichloride complex, $Cp^*Cp'''ZrCl_2$ (**3-Cl$_2$**), was accomplished in 38% yield by refluxing LiCp‴ with Cp^*ZrCl_3 for 3 days in THF followed by extraction with diethyl ether. Single crystals of air- and moisture-stable **3-Cl$_2$** were obtained from slow evaporation of a concentrated solution of the metallocene in a 75:25 diethyl ether:pentane mixture. The solid-state structure of **3-Cl$_2$**, as determined by X-ray diffraction, is shown in Figure 1 and contains two independent, enantiomeric molecules in the unit cell. In both enantiomers, the [$SiMe_3$] groups are oriented to minimize unfavorable steric interactions in the narrow ("back") portion of the metallocene wedge and with the chloride ligands.

The desired isobutyl hydride complex, **3**, was prepared by adding 2 equiv of $LiCMe_3$ to $Cp^*Cp'''ZrCl_2$. Samples prepared using this method are invariably contaminated with the cyclometalated zirconocene, Cp*(η^5-C_5H_2-2,4-$(SiMe_3)_2$-1-η^1-$SiMe_2$-CH_2)ZrH (**3a**), resulting from facile reductive elimination of isobutane (Scheme 1). To obtain pure **3**, a low temperature synthetic route that suppressed reductive elimination was sought. Insertion of isobutene into the corresponding zirconocene dihydride was an attractive route, as these reactions often proceed rapidly at low temperature.[37] The metastable zirconocene dihydride, $Cp^*Cp'''ZrH_2$ (**6**), was prepared by adding 1 atm of H_2 gas to the mixture of **3** and **3a** at 22 °C. Although stable under an atmosphere of dihydrogen for extended periods, **6** reverts to **3a** upon removal of the H_2 atmosphere, precluding efforts to isolate the molecule in the solid state. Despite this complication, preparation of pure **3** was achieved via addition of 1 equiv of isobutene to **6** at low temperature (Scheme 1).

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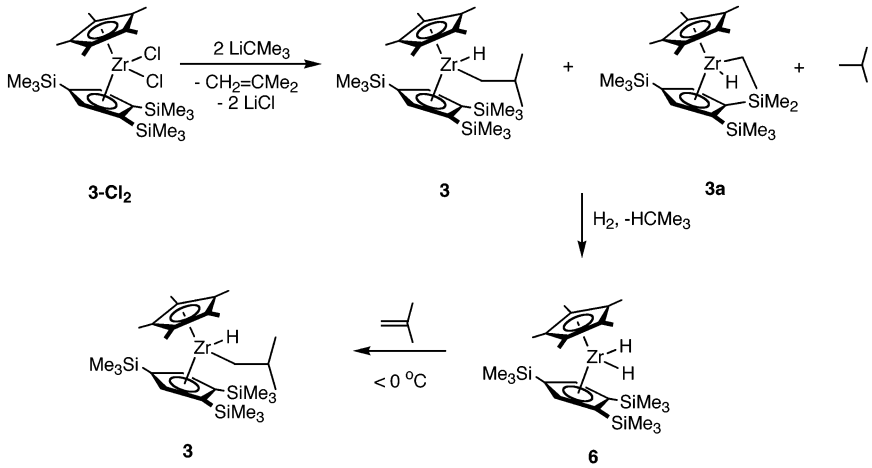
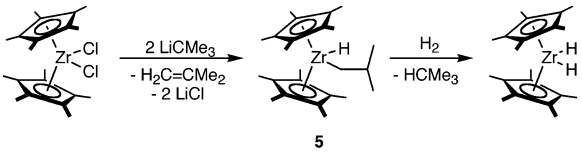
Scheme 1

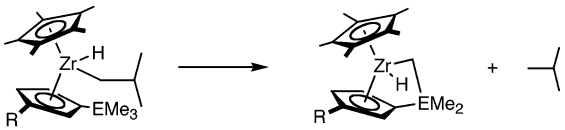


In a similar procedure, Cp*(^{t}BuCp)Zr(CH_2CHMe_2)H (**4**, ^{t}BuCp = η^5-C_5H_4-(CMe_3)) was synthesized by adding 1 equiv of isobutene to [Cp*(^{t}BuCp)ZrH_2]$_2$.[38] To complete the series of zirconocene isobutyl hydride complexes, Cp*$_2$Zr-(CH_2CHMe_2)H (**5**) was also prepared. Although **5** has been prepared previously by reacting isobutene with Cp*$_2ZrH_2$,[30] addition of 2 equiv of $LiCMe_3$ to Cp*$_2ZrCl_2$ proved to be a more efficient route. Using this methodology, we prepared **5** in 92% yield in a one-pot synthesis in less than 1 h, unlike the previous multistep procedure which requires several days.[30] Hydrogenation of **5** to Cp*$_2ZrH_2$ proceeded in a few minutes at 1 atm of H_2 and ambient temperature, also a significant improvement over previously reported procedures (eq 2).[39]



(2)

Relative Rates of Reductive Elimination. Monitoring the thermal stability of each of the zirconocene isobutyl hydride complexes, **1**−**4**, by ^{1}H NMR spectroscopy revealed that each molecule undergoes smooth first-order elimination of isobutane along with formation of a cyclometalated zirconocene hydride. The observed reactions are best viewed as a composite of a reductive elimination process liberating alkane followed by oxidative addition of a C−H bond of one of the cyclopentadienyl substituents to yield the cyclometalated product. Thus, **1** converted to Cp*(η^5-C_5H_4-η^1-$SiMe_2CH_2$)ZrH (**1a**) and **2** reacted to yield Cp*(η^5-C_5H_3-3-$SiMe_3$-η^1-$SiMe_2CH_2$)ZrH (**2a**) and likewise **3** to **3a** (eq 3). The *tert*-butyl substituted zirconocene, **4**, also undergoes thermal reductive elimination of isobutane to yield Cp*(η^5-C_5H_4-η^1-CMe_2CH_2)ZrH (**4a**) in a first-order process, although other unidentified side products are also formed. It is important to mention that, for **2**, the presence of different diastereotopic [$SiMe_3$] substituents offers the possibility of two cyclometalated hydride products. For **3**, three such isomers are possible. In both cases, only one isomer was observed by ^{1}H and ^{13}C NMR spectroscopy. Identification of the preferred diastereomers and the origin of their formation are deferred to a later section in the article.



(3)

1: R = H, E = Si
2: R = $SiMe_3$, E = Si
4: R = H, E = C

1a: R = H, E = Si
2a: R = $SiMe_3$, E = Si
4a: R = H, E = C

The experimentally determined first-order rate constants measured at 40 °C for **1**−**5** are shown in Table 1. This temperature was selected because each of the reductive elimination reactions occurs at a rate that is convenient to measure by ^{1}H NMR spectroscopy. Rate constants were measured as a function of temperature for isobutane formation from the thermolysis of **2** over a 55° temperature range (19−74 °C). An excellent fit to the Eyring equation was obtained (R^2 = 0.997), yielding activation parameters of $\Delta H^{\ddagger} = 25(1)$ kcal/mol and $\Delta S^{\ddagger} = 3(3)$ eu. The entropy of activation is consistent with a unimolecular reaction.

In related processes, the dihydride complexes, **6** and Cp*Cp″ZrH_2 (**7**), underwent loss of dihydrogen and formation of the corresponding cyclometalated hydride complexes, **3a** and **2a**, respectively. Qualitatively, the rates of reductive elimination for these complexes follow the same trend as those observed for the isobutyl hydride complex, where **6** undergoes more rapid expulsion of dihydrogen than **7**. In both cases, the reductive elimination reactions are substantially faster than those for the alkyl hydride complexes, in contrast to previous reports for **5** and Cp*$_2ZrH_2$.[30,40]

The kinetic data demonstrate the modest effect of cyclopentadienyl ligand substitution on the rate of reductive elimination of isobutane. The most salient trend is the steady increase observed in the rate constant as [$SiMe_3$] groups are introduced onto the cyclopentadienyl ligands. For example, addition of one [$SiMe_3$] group in going from **1** to **2** resulted in a 5-fold rate enhancement, whereas further silylation (**2** to **3**) induced a 40-fold increase in rate constant. This trend is opposite to those previously reported for olefin insertion and β-hydrogen elimination, where increased ancillary ligand substitution results in slower rates of reaction.[41]

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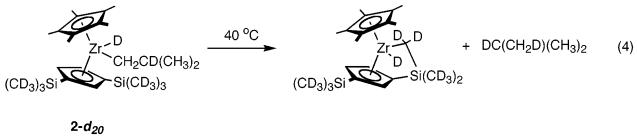
Table 1. First-Order Rate Constants for the Series of Zirconocene Isobutyl Hydride Complexes at 40 °C

compound	k (s^{-1})	relative rate
1	$1.6(3) \times 10^{-5}$	5.0
2	$7.8(2) \times 10^{-5}$	24
3	$3.1(1) \times 10^{-3}$	970
4	$7.7(2) \times 10^{-6}$	2.4
5	$3.2(5) \times 10^{-6}$	1

Isotopic Labeling Studies. To account for the observed cyclopentadienyl ligand effects and to elucidate the mechanism for reductive elimination, a series of isotopic labeling studies were conducted. The simplest possible mechanism, termed the "direct pathway", involves straightforward combination of the zirconocene hydride and the coordinated alkyl to form the C−H bond of the resulting alkane. To test this possibility, Cp*Cp″Zr-($CD_2CD(CD_3)_2$)D (**2-*d*$_{10}$**) was prepared in 90% yield and >95% isotopic purity by addition of $LiC(CD_3)_3$ to a toluene solution of Cp*Cp″$ZrCl_2$. Thermolysis of **2-*d*$_{10}$** at 40 °C yielded $DC(CD_2H)(CD_3)_2$ and the cyclometalated zirconocene complex (Scheme 2). Analysis of the resulting zirconocene by $^2H\{^1H\}$ NMR spectroscopy demonstrated that isotopic exchange had occurred in the zirconocene hydride and in all positions of the cyclometalated [$SiMe_3$] moiety. Continued thermolysis of the cyclometalated product resulted in isotopic exchange into the other [$SiMe_3$] group over the course of hours, demonstrating the kinetic accessibility of the other diastereomeric cyclometalated hydride (vide infra). If the direct mechanism were operative, only isobutane-d_{10} and the cyclometalated zirconocene hydride, free of deuterium incorporation, would be formed. The observed isotopic exchange definitively excludes this mechanistic possibility.

Because the thermolysis of **2-*d*$_{10}$** and literature precedent[30] suggested the participation of the cyclopentadienyl ligand substituents in the reductive elimination process, additional isotopic labeling studies were conducted. Reaction of Cp*(η^5-C_5H_3-1,3-($Si(CD_3)_3)_2$)ZrD_2 (vide infra) with 1 equiv of isobutene afforded Cp*(η^5-C_5H_3-1,3-($Si(CD_3)_3)_2$)Zr(CH_2CDMe_2)D (**2-*d*$_{20}$**)- in >95% isotopic purity (^1H and ^2H NMR) (Scheme 3). Warming benzene-d_6 solutions of the complex to 40 °C induced reductive elimination, forming $DC(CH_2D)(CH_3)_2$ and the cyclometalated zirconocene with no isotopic exchange (eq 4). Because direct reductive elimination has been previously excluded, this result clearly establishes the [$SiMe_3$] groups as the source of hydrogen (or deuterium) for the C−H bond forming reaction.



Previous work with **5** suggested that the mechanism for reductive elimination proceeds by initial zirconium-to-ring hydrogen transfer followed by rate-determining oxidative addition of a cyclopentadienyl methyl group (Scheme 4).[30] The isotopic labeling studies with **2** are consistent with this general process, although chemically inequivalent cyclopentadienyl rings complicate the mechanism for reductive elimination, as each may have its own preference for hydrogen transfer and cyclometalation.

To establish the propensity for [Me] versus [$SiMe_3$] group participation, isotopic labeling studies were conducted with the zirconocene dideuteride, Cp*Cp″ZrD_2 (**7-*d*$_2$**). Preparation of this molecule was easily accomplished via addition of 1 atm of D_2 gas to **7** at 22 °C. Instantaneous deuterium for hydrogen exchange was observed in the metal hydride positions. Continued monitoring by $^2H\{^1H\}$ NMR spectroscopy revealed deuterium incorporation into the [$SiMe_3$] substituents over the course of 2 h (Scheme 3). Complementary ^1H NMR studies revealed essentially complete deuteration of these groups after 24 h. Significant deuterium incorporation into the [C_5Me_5] ring took place only after 3 days at 22 °C. The absolute rate of isotopic exchange, not the relative selectivity, is dependent on the D_2 pressure employed. Addition of 4 atm of D_2 to a pentane solution of **7** resulted in slower isotopic exchange than the corresponding reaction at 1 atm. This concentration effect argues against σ-bond methathesis pathways. Preferential [$SiMe_3$] isotopic exchange, coupled with the observation that the [$SiMe_3$] substituent is the source of hydrogen (or deuterium) for the liberated alkane, clearly establishes the preference for [$SiMe_3$] group activation and cyclometalation over the methyl groups from the [C_5Me_5] ligand.

Selectivity in the zirconium-to-ring hydrogen transfer step (i, Scheme 4) is also complicated with mixed-ring zirconocene complexes. Formally, this process may be considered a reductive elimination reaction providing a zirconium(II) complex containing a neutral cyclopentadiene ligand. As a result of the formal two-electron reduction at the metal, the hydrogen migration may, therefore, be viewed as a proton-transfer reaction. Protonation of the [C_5Me_5] over the [Cp″] ring would be expected because it is well established that silylated cyclopentadienes are more acidic than their alkylated counterparts.[42]

Identifying the rate-determining step for the alkane elimination-cyclometalation process is essential to understanding the origin of the observed substituent effects. Although the identity of this transformation has been the subject of speculation, it has yet to be experimentally verified. To address this issue, the kinetic isotope effect for reductive elimination was measured using two independent methods. For these experiments, the isotopically labeled zirconocene, Cp*(η^5-C_5H_3-1,3-($Si(CD_3)_3)_2$)-Zr(CH_2CHMe_2)H (**2-*d*$_{18}$**), was prepared via the synthetic route shown in Scheme 5. Deuteration of **7** with D_2 gas followed by treatment with DCl afforded the deuterated zirconocene dichloride, Cp*(η^5-C_5H_3-1,3-($Si(CD_3)_3)_2$)$ZrCl_2$. Subsequent treatment with 2 equiv of $LiCMe_3$ yielded **2-*d*$_{18}$**. A primary isotope effect (k_H/k_D) of 3.3(3) was measured at 60 °C using the average of five independent trials for the reductive elimination of both **2** and **2-*d*$_{18}$**. Measurement of the isotope effect using a more reliable internal competition experiment, whereby an equimolar mixture of **2** and **2-*d*$_{18}$** was thermolyzed at 60 °C, provided a similar value of 3.6(3). A primary isotope effect arising from introduction of isotopic labels into the [$SiMe_3$] substituents suggests that reductive elimination proceeds via rapid zirconium-to-ring hydrogen transfer followed by rate-determining cyclometalation (ii, Scheme 4).

Knowledge of the rate-determining step allows for the explanation of the observed substituent effects on the rate of isobutane reductive elimination. Because cyclometalation of a

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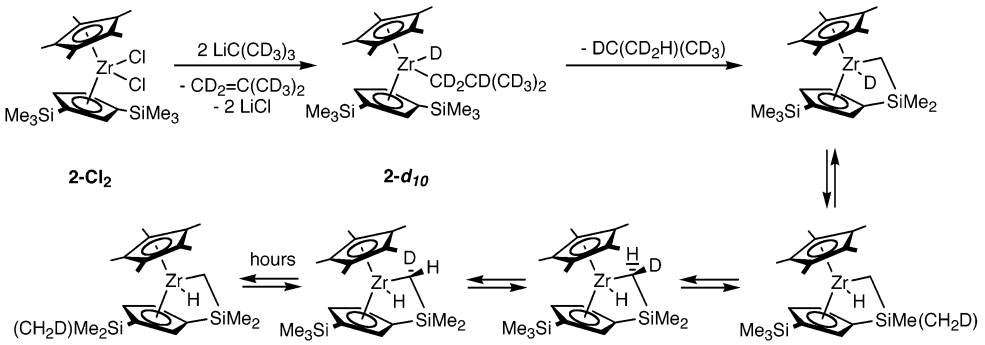
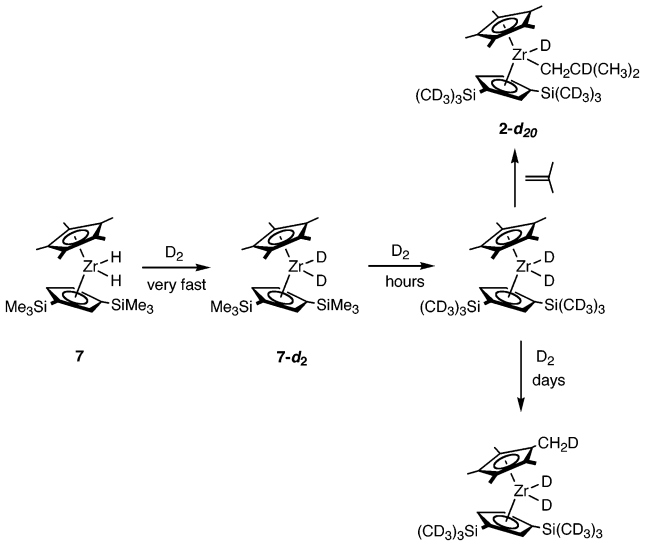
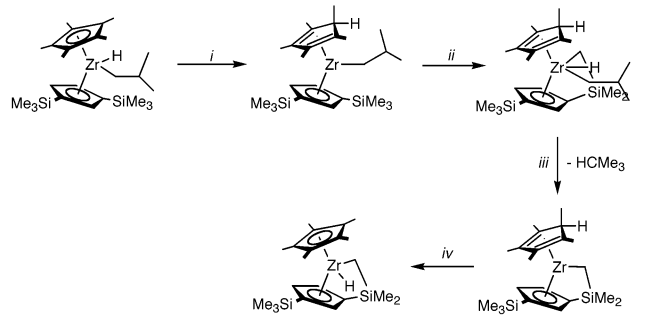
Scheme 2



Scheme 3



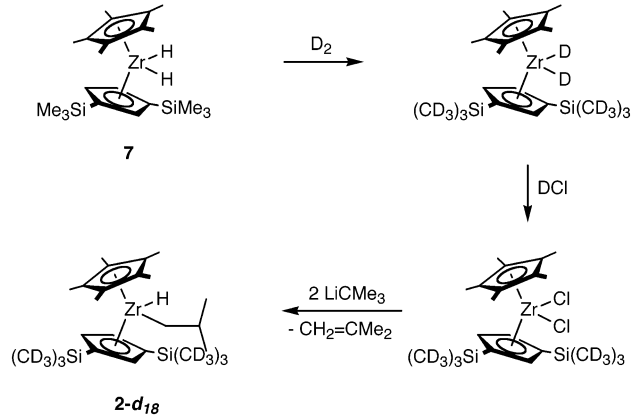
Scheme 4



cyclopentadienyl substituent is the slow step, zirconocenes such as **1** and **4** that contain readily available C−H bonds for oxidative addition are expected to undergo more facile alkane elimination as compared to **5**. The modest increase in the rate of reductive elimination of **1** as compared to **5** may be attributed to the known preference for oxidative addition of β-silicon C−H bonds over purely alkyl substituents.[43]

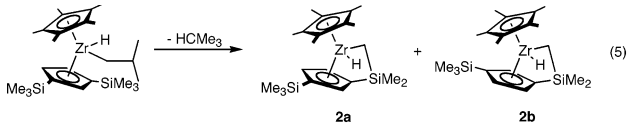
Comparing the relative rates of **1** and **2** demonstrates that the presence of additional [$SiMe_3$] groups results in more facile reductive elimination reactions. This moderate enhancement may be attributed to a statistical effect, where **2** simply has more C−H bonds available for rate-determining oxidative addition. However, this explanation does not account for understanding the nonlinear, 40-fold increase in the rate of reductive elimination observed for **3** as compared to **2**. The additional silylation may serve to provide a conformer with accessible C−H bonds for oxidative addition (vide infra, Scheme 6).

Scheme 5



One final point regarding the mechanism proposed in Scheme 4 concerns the possibility of transferring the hydrogen to the same ring that undergoes cyclometalation. If this were the case, the rate of reductive elimination for **2** and $Cp''_2Zr(CH_2CHMe_2)H$ (**8**) would be similar, because the other "innocent" cyclopentadienyl group should have little effect on the rate. As will be presented later in the article, **8** undergoes more facile reductive elimination than **2**, suggesting that this mechanism is not operative.

Solution Structures of the Cyclometalated Hydride Complexes 2a and 3a. As mentioned previously, reductive elimination of isobutane from **2** can afford, in principle, two diastereomeric cyclometalated hydride complexes, **2a** and **2b** (eq 5). During the course of isobutane reductive elimination from **2**, only one isomer (**2a**) is observed by ^1H and ^{13}C NMR spectroscopy. Continued thermolysis at 74 °C for several days allows for the observation of significant quantities (∼40%) of **2b**.



(5)

Diastereomer **2a** was identified using a combination of NOE difference and NOESY NMR spectroscopy in benzene-d_6 (Table 2). Correlation between the zirconium hydride and the doublet centered at −4.20 ppm identifies this resonance as the syn (relative to the zirconium hydride) Zr−CH_2 hydrogen. No correlation is observed between the zirconium hydride and the

(43) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

Scheme 6

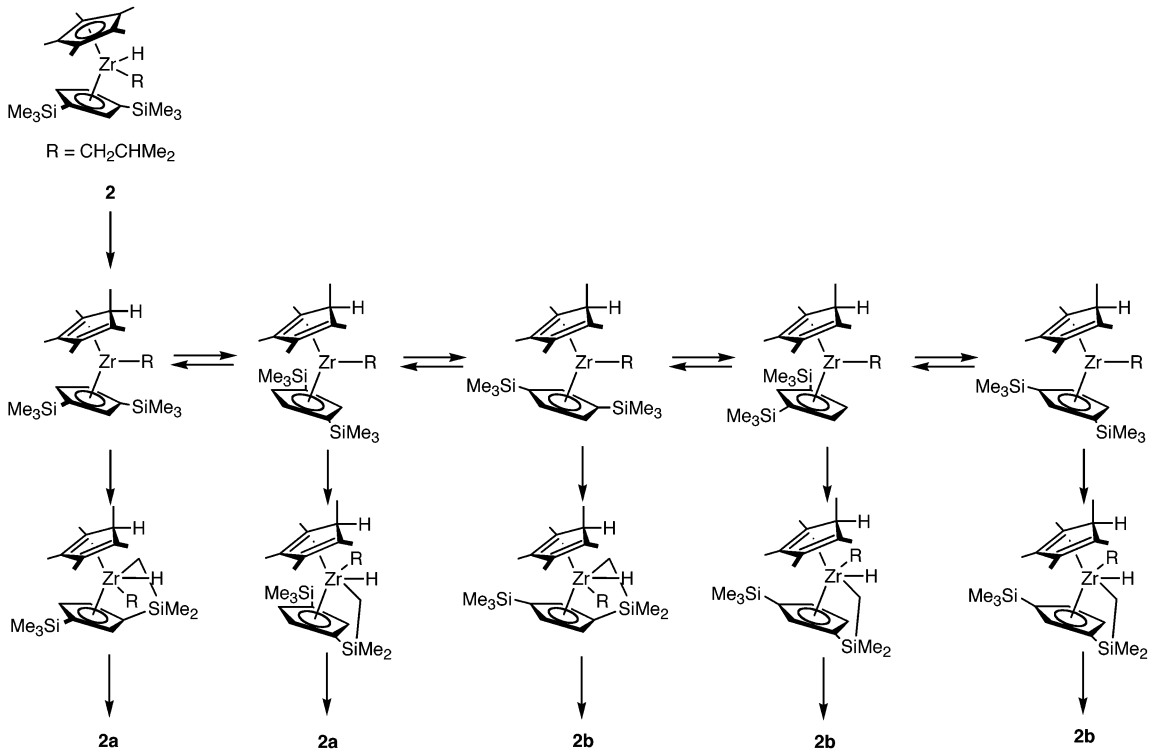
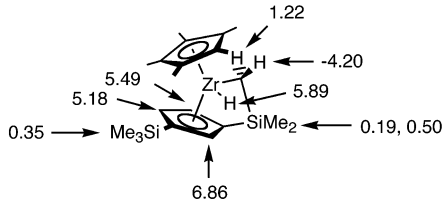


Table 2. Select NOE and NOESY Data for **2a** in Benzene-d_6



2a

peak irradiated (ppm)	peak enhanced (ppm)
syn-Zr−CH_2 (−4.20)	Zr−H (5.89), Cp (6.86), Zr−CH_2 (1.22), $SiMe_2$ (0.19)
Zr−H (5.89)	Cp (6.86), Zr−CH_2 (−4.20), $SiMe_2$ (0.19), $SiMe_3$ (0.35)
Cp (6.86)	Zr−H (5.89), $SiMe_2$ (0.19), $SiMe_3$ (0.35), Zr−CH_2 (−4.20)
Cp (5.49)	$SiMe_2$ (0.50), Cp (5.18)

anti Zr−CH_2 doublet centered at 1.22 ppm. Both the zirconium hydride and the syn methylene hydrogen correlate with only one of the cyclopentadienyl hydrogens (6.86 ppm), which itself does not correlate with any other Cp peaks. These data, along with other supporting correlations (Table 2), demonstrate that the isomer formed is **2a** rather than **2b**.

A mechanism that accounts for the possibility of different diastereomeric cyclometalated compounds is shown in Scheme 6. Oxidative addition from different conformers of the [$SiMe_3$]-substituted cyclopentadienyl ring accounts for the formation of the different diastereomers. Conformers that ultimately lead to **2a** orient the [$SiMe_3$] substituents toward the metallocene wedge, thus avoiding unfavorable inter-ring steric interactions. Isotopic labeling experiments (Scheme 2) along with thermolysis studies indicate that diastereomer **2b** is kinetically accessible.

The cyclometalated hydride (**3a**), arising from reductive elimination of isobutane from **3**, has three possible isomers (eq 6). As with **2a**, only one was detected by ^{1}H and ^{13}C NMR spectroscopy. Addition of aqueous DCl to a benzene-d_6 solution of **3a** and analysis of the resulting zirconocene dichloride by ^{2}H{^{1}H} NMR spectroscopy provided a single resonance at 0.43 ppm corresponding to the equivalent (rather than unique) [$SiMe_3$] groups of **3-Cl$_2$**. Similarly, addition of 1 atm of D_2 gas placed the isotopic label only in the equivalent [$SiMe_3$] groups. From these experiments, cyclometalation of the unique [$SiMe_3$] group is excluded, thus eliminating the possibility of **3c** for the observed cyclometalated hydride.

As with **2a**, NOE difference NMR spectroscopy was employed to differentiate between the diastereomers, **3a** and **3b**. Correlation between the cyclopentadienyl multiplet at 8.05 ppm and both [$SiMe_3$] substituents allows for the assignment of this resonance to the Cp hydrogen between these groups. This hydrogen also correlates with the zirconocene hydride peak (6.17 ppm) as well as one methyl group of the cyclometalated [$SiMe_2$] moiety. On the basis of these data and on other more subtle NOE enhancements, we tentatively assign the observed isomer as **3a**.

Application of Reductive Elimination to Dinitrogen Activation. The observed rate enhancement provided by the incorporation of [$SiMe_3$] substituents suggested that highly silylated zirconocenes may undergo facile reductive elimination and coordination of dinitrogen. Such methodology may allow for the preparation of zirconium dinitrogen complexes inaccessible by traditional alkali metal reduction routes as well as provide a reproducible and relatively mild protocol for the preparation of N_2 complexes. For these reasons, the synthesis

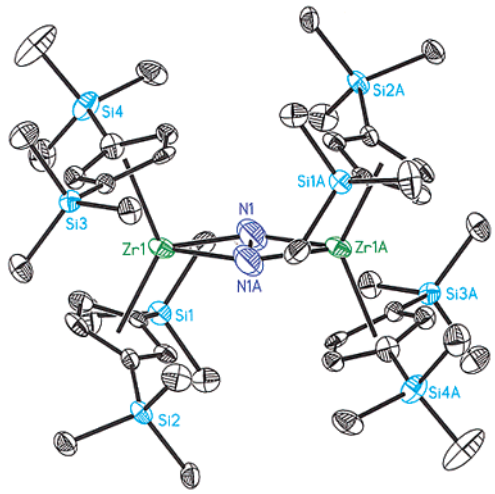
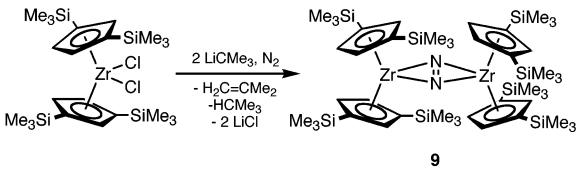


Figure 2. Molecular structure of **9** with 30% probability ellipsoids. Selected bond distances (Å): N(1)−N(1A) = 1.47(3); Zr(1)−N(1) = 2.118(16); Zr(1)−N(1A) = 2.110(19). Selected angles (deg): N(1A)−Zr−N(1) = 40.6(9); N(1A)−N(1A)−Zr(1A) = 70.0(14); N(1A)−N(1A)−Zr = 69.4(12); Zr(1A)−N(1)−Zr(1) = 139.4(9).

of **8** and the chemistry arising from reductive elimination of isobutane were pursued.

Addition of 2 equiv of $LiCMe_3$ to Cp''_2ZrCl_2 resulted in facile extrusion of isobutane and allowed for the isolation of dark purple crystals, identified as the dinitrogen complex, $[Cp''_2Zr]_2$-(μ_2-η^2, η^2-N_2) (**9**), albeit in low (10%) yield (eq 7). Single-crystal X-ray diffraction on purple needles of **9** obtained from pentane revealed a dimeric structure with a bridging, side-on dinitrogen fragment contained in a planar Zr_2N_2 core (Figure 2). Side-on coordination of the N_2 ligand in **9** is noteworthy because this once rare coordination mode is now emerging as the preferred bonding arrangement in zirconium dinitrogen complexes[8] and has also been observed in several similar lanthanide N_2 compounds.[44−46] Side-on coordination of the dinitrogen ligand appears to be important for the reduction of the dinitrogen ligand because the N−N bond distance of 1.47 (3) Å in **9** is the longest observed in any metallocene dinitrogen complex and is comparable to the N−N bond length in hydrazine and other zirconium amido-phosphine ligated compounds.[47−49] It should be noted that in one side-on bound dinitrogen complex, $[Cp^*_2Sm]_2$(μ_2, η^2, η^2-N_2), an anomalously short N−N bond length is observed.[44]

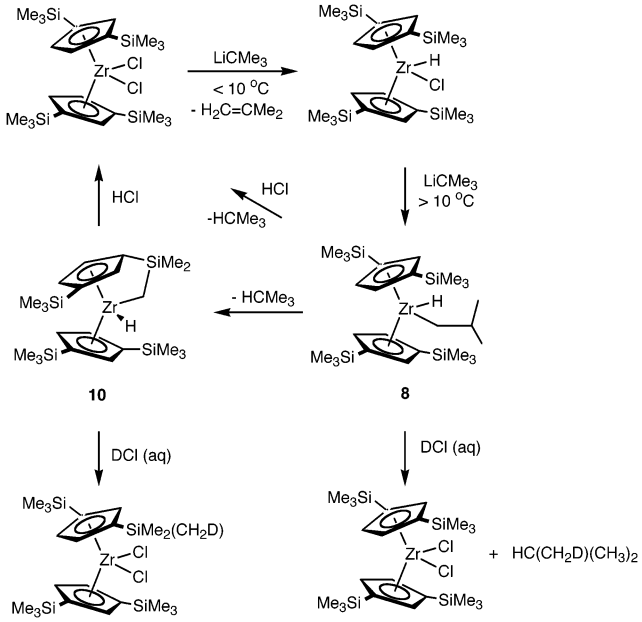


(7)

9

Unlike previously reported dimeric zirconocene dinitrogen complexes, **9** is paramagnetic.[50] Solution magnetic susceptibility

Scheme 7



(Evans method) yields a magnetic moment of 2.73 μB, consistent with a ground-state triplet containing two formally Zr(III), d^1 centers. The Zr−Zr distance of 3.996 Å is in accord with the observed magnetism because such a distance is outside the range typically observed for bimetallic antiferromagnetic coupling.[13]

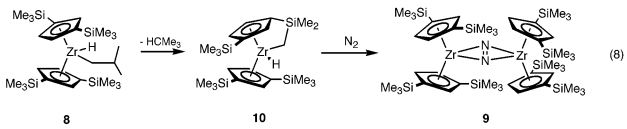
Elucidating the Origins of 9. Several experiments were conducted to elucidate the origins of **9**. Addition of toluene-d_8 to a mixture of Cp''_2ZrCl_2 and 2 equiv of $LiCMe_3$ at −78 °C resulted in formation of $Cp''_2Zr(H)Cl$,[36] free isobutylene, and excess $LiCMe_3$. As determined by variable temperature ^1H NMR spectroscopy, these products persisted until the sample was warmed to 10 °C, upon which a second alkylation, accompanied by isomerization, occurred forming **8** in near quantitative yield (Scheme 7). At temperatures below 22 °C, **8** is stable for several minutes, eventually undergoing reductive elimination of isobutane and forming a cyclometalated zirconocene hydride (**10**). As with **2a** and **3a**, two diastereomers are possible, although the reactivity of this molecule has precluded structural assignment. Simply mixing Cp''_2ZrCl_2 and 2 equiv of $LiCMe_3$ at 22 °C and following the course of the reaction at short time intervals by ^1H NMR spectroscopy produced similar observations. At 22 °C, the conversion of **8** to **10** with concomitant formation of isobutane takes place with a rate constant of 2(2) $\times$ 10^{-4} s^{-1}.

The instability of both **8** and **10** prompted several additional experiments to further establish their identity. Addition of excess HCl (as a 2.0 M solution in diethyl ether) to a mixture of **8** and **10** afforded isobutane (1 equiv per equiv of **8**) along with analytically pure Cp''_2ZrCl_2 (Scheme 7). No other zirconocene complexes or organic products were observed. In a similar experiment, aqueous DCl was added to the same mixture, resulting in formation of $HC(CH_2D)(CH_3)_2$ and the zirconocene dichloride. Deuterium incorporation into the $[SiMe_3]$ groups of the ligand array was confirmed by $^2H\{^1H\}$ NMR spectroscopy arising from the fraction of the mixture present as **10** (Scheme

(44) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
(45) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7927.
(46) Evans, W. J.; Allen, N. T.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 359.
(47) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.
(48) Cohen, J. D.; Mylvaganam, M.; Fryzuk, M. D.; Loehr, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 9529.
(49) Cohen, J. D.; Fryzuk, M. D.; Loehr, T. M.; Mylvaganam, M.; Rettig, S. J. *Inorg. Chem.* **1998**, *37*, 112.
(50) Jeffery, J.; Lappert, M. F.; Riley, P. I. *J. Organomet. Chem.* **1979**, *181*, 25−36.

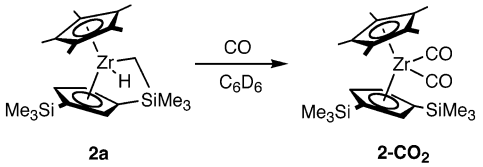
7). Also in accord with this observation, addition of HCl to a benzene-d_6 solution of **10** resulted in clean formation of Cp''_2ZrCl_2 with no other detectable products. Although dihydrogen was anticipated, the dilute conditions (0.02 M) under which these experiments were performed have not permitted its detection. Exposure of the mixture of **8** and **10** to 1 atm of hydrogen gas resulted in immediate formation of isobutane accompanied by decomposition of the zirconocene. This facile decomposition pathway, in conjunction with the poor solubility of N_2 in organic solvents such as pentane, may explain why **9** is isolated in such poor yield. Several attempts were made to either isolate or observe Cp''_2ZrH_2, all of which have been unsuccessful. Likewise, attempts to isolate either **8** or **10** in the solid state by removing the toluene in vacuo resulted in increased rates of decomposition.

Exposing toluene solutions of **10** to an atmosphere of dinitrogen at −35 °C resulted in formation of the dinitrogen complex, **9**. Because **9** forms over several days at −35 °C and the lifetime of **8** under the same conditions is only a few hours, the dinitrogen complex does not form directly from reductive elimination of isobutane from **8** but rather from the reaction of N_2 with the cyclometalated hydride, **10** (eq 8). Thus, the cyclometalated hydride, **10**, provides a masked-form of low-valent zirconium that can activate dinitrogen.



(8)

Scope of Dinitrogen Activation with Cyclometalated Zirconocene Hydride Complexes. Because the cyclometalated hydride, **10**, provided a unique entry into the zirconocene dinitrogen chemistry, the related complexes, **1a**−**4a**, were evaluated for similar reactivity. Allowing pentane solutions of **1a**−**4a** to stand under an atmosphere of N_2 at −35 °C or ambient temperature did not result in the formation of the corresponding dinitrogen complexes over the course of weeks. However, addition of 1 atm of carbon monoxide to a benzene-d_6 solution of **2a** resulted in clean and quantitative formation of $Cp^*Cp''Zr(CO)_2$ (**2-(CO)$_2$**). Thus, addition of a ligand that is effective in stabilizing Zr(II) demonstrates that **2a**, like **10**, may serve as a masked source of low-valent zirconium. Addition of CO to the isobutyl hydride, **2**, resulted in a mixture of products arising from both carbon monoxide insertion and ligand-induced reductive elimination.[51]



(9)

Although **2a** may serve as a source of Zr(II), it is still curious why this molecule and the other mixed-ring cyclometalated zirconocene hydrides are unreactive toward dinitrogen. One important observation is that in the absence of N_2, **10**, unlike **1a**−**4a**, undergoes decomposition, demonstrating the inherent instability of this molecule relative to other cyclometalated zirconocene hydrides.

Table 3. Infrared Stretching Frequencies for Relevant Zirconocene Dicarbonyl Complexes in Pentane Solution[a]

complex	$\nu(CO)_{sym}$ (cm^{-1})	$\nu(CO)_{asym}$ (cm^{-1})	$\nu(CO)_{av}$ (cm^{-1})
$Cp^*_2Zr(CO)_2$[52]	1946	1853	1900
$Cp^*Cp''(CO)_2$	1954	1865	1910
$Cp''_2Zr(CO)_2$[52]	1967	1881	1924
11-(CO)$_2$[52]	1969	1883	1926
13-(CO)$_2$	1967	1888	1928

[a] Previously reported values were taken from ref 52.

The origin of the ground-state destabilization of **10** relative to **1a**−**4a** may be rationalized on the basis of cyclopentadienyl electronic effects. The electron donating ability of the $[C_5Me_5]$ ligand relative to [Cp″] provides electronic stabilization of the Zr(IV) ground state for the mixed ring complexes, increasing the barrier toward N_2 activation. Recent studies by Parkin[52] corroborate these findings. Infrared stretching frequencies of the zirconocene dicarbonyl complex were found to be an effective measure for assaying the electronic environment imparted by the cyclopentadienyl substituents. The pentane solution carbonyl stretching frequencies for the zirconocenes relevant to this study are contained in Table 3. The zirconocene with the most electron donating ligand set, $Cp^*_2Zr(CO)_2$,[52] displays CO stretching frequencies at 1946 and 1853 cm^{-1}, suggesting substantial electron donation from the $[C_5Me_5]$ rings resulting in stabilization of the Zr(IV) ground state. For the silylated zirconocene, $Cp''_2Zr(CO)_2$, values of 1967 and 1881 cm^{-1} were reported,[52] demonstrating an electronically destabilized ground state relative to $[Cp^*_2Zr]$. The mixed ring complex, $Cp^*Cp''Zr(CO)_2$, displays intermediate stretching frequencies of 1954 and 1865 cm^{-1}, suggesting one $[C_5Me_5]$ provides sufficient ground-state stabilization to inhibit N_2 activation.

Elucidation of the mechanism for reductive elimination (Scheme 4) and the origin of dinitrogen activation by **10** (eq 8) allows for the explanation of the relative stabilities of other zirconocene alkyl hydride and dihydride complexes. For example, the monomeric *ansa*-zirconocene dihydride, *rac*-$Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}(SiMe_3)\text{-}4\text{-}CMe_3)_2ZrH_2$ (**11**), was shown, albeit serendipitously, to undergo facile extrusion of dihydrogen and activation of dinitrogen to afford *rac*-$[Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}(SiMe_3)\text{-}4\text{-}CMe_3)_2Zr]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$ (**12**) (Figure 3).[53] We recently reported a related zirconocene, $^iPr_2Si(\eta^5\text{-}C_5H_2\text{-}3,4\text{-}(SiMe_3)_2)(\eta^5\text{-}C_5H_3\text{-}3\text{-}(SiMe_3))Zr(CH_2CHMe_2)H$ (**13**), that is stable to reductive elimination even at temperatures of 40 °C.[36] Comparing the carbonyl stretching frequencies for $Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}(SiMe_3)\text{-}4\text{-}CMe_3)_2Zr(CO)_2$ (**11-(CO)$_2$**, 1969 and 1883 cm^{-1})[52] and $^iPr_2Si(\eta^5\text{-}C_5H_2\text{-}3,4\text{-}(SiMe_3)_2)(\eta^5\text{-}C_5H_3\text{-}3\text{-}(SiMe_3))Zr(CO)_2$ (**13-(CO)$_2$**, 1967 and 1888 cm^{-1}) reveals that the electronic environment imparted by the ancillary ligands is essentially identical and is similar to **8**. However, each complex displays different reactivity toward N_2. This difference is attributed to the accessibility of the substituent C−H bonds for oxidative addition. For **11**, incorporation of $[SiMe_3]$ groups adjacent to

(51) Pool, J. A.; Chirik, P. J., unpublished results.

(52) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G. E.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525.

(53) Chirik, P. J.; Henling, L. M.; Bercaw, J. E. *Organometallics* **2001**, *20*, 534.

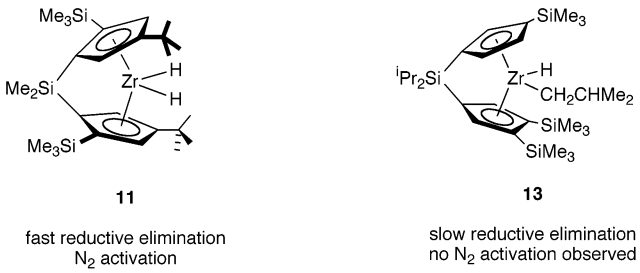


Figure 3. Relative rates of reductive elimination and dinitrogen activation as a function of ligand array for *ansa*-zirconocenes.

the *ansa* bridge provides C−H bonds that are in proximity to the vacant $1a_1$ molecular orbital required for cyclometalation. For **13**, where sluggish rates of reductive elimination are observed, the [$SiMe_3$] groups are oriented away from the metallocene wedge, providing a high activation barrier for oxidative addition.

Concluding Remarks

The rate of reductive elimination for a family of zirconocene alkyl hydride complexes was measured and found to increase with incorporation of substituents that undergo facile cyclometalation. Isotopic labeling studies firmly establish that the mechanism of these reactions proceeds via reversible zirconium-to-ring hydrogen transfer followed by rate-determining oxidative addition of a cyclopentadienyl ligand substituent. Application of this mechanistic data has led to the preparation of a highly silylated zirconocene isobutyl hydride complex that undergoes facile thermal reductive elimination and coordination of dinitrogen. More detailed experiments indicate that the dinitrogen activation occurs from reaction of N_2 with a destabilized cyclometalated zirconocene hydride rather than resulting directly from reductive elimination of the alkyl hydride. These results provide one of the first examples of mechanistically well-established activation of dinitrogen by a group 4 transition metal compound and may result in the synthesis of new ligand motifs that allow predictable and reproducible entry into the rich chemistry of low-valent zirconocenes.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using a standard vacuum line, Schlenk and cannula techniques, or in an M. Braun drybox under an atmosphere of purified nitrogen or argon. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive reactions were dried and deoxygenated using literature methods.[54] Benzene-d_6, toluene-d_8, and deuterium gas were purchased from Cambridge Isotope Laboratories. The benzene-d_6 was distilled from sodium metal under argon and stored over 4 Å molecular sieves, whereas the toluene-d_8 was stored over sodium metal and vacuum transferred immediately before use. Both hydrogen and argon gas were purchased from Airgas Inc. and passed through columns of 4 Å molecular sieves and Ridox before admission into a high vacuum system. Celite was purchased from Aldrich, stored at 140 °C, and dried for 24 h under high vacuum at 150 °C.

^{1}H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz, whereas ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer operating at 100.511 MHz. All reported chemical shifts are relative to TMS using ^{1}H (residual) or ^{13}C NMR chemical shifts of the solvent as a secondary standard. ^{2}H NMR spectra were recorded at 61.354 MHz on a Varian VXR-400 spectrometer and referenced with an internal benzene-d_6 standard. Single crystals of **3-Cl$_2$** and **9** suitable for X-ray diffraction data were coated with polyisobutylene in the drybox and quickly transferred onto the goniometer head of a Siemens SMART CCD area detector system equipped with a fine-focus molybdenum X-ray tube (λ = 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. Magnetic susceptibility was determined by Evans method[58] using Cp_2Fe as a standard in benzene-d_6 solution. Robertson Microlit Labs, Inc., Madison, New Jersey, carried out elemental analyses.

Preparation of Cp*Cp′$ZrCl_2$,[55] **2**,[36] **2a**, Cp*$ZrCl_3$,[56] **4**,[38] $LiCH_2CHMe_2$,[57] and LiCp‴[42] were accomplished as described previously. Preparation of $LiC(CD_3)_3$ was accomplished using a modified procedure[57] for $LiCMe_3$ with $ClC(CD_3)_3$ purchased from Cambridge Isotope Laboratories. Cp*$_2ZrCl_2$ was purchased from Strem Chemicals, and 1.5 M $LiCMe_3$ in pentane and 1.6 M $LiCH_2CH_2CH_2CH_3$ in hexane were purchased from Acros Organics. These reagents were used as received. Isobutylene was purchased from Aldrich Chemical Co., dried over activated 4 Å molecular sieves, and vacuum transferred prior to use.

Preparation of Cp*Cp′Zr(CH_2CHMe_2)H (1). In the drybox, a 20 mL scintillation vial was charged with 0.108 g (0.249 mmol) of Cp*Cp′$ZrCl_2$ and approximately 10 mL of toluene. The clear yellow solution was frozen in the cold well. To the thawing stirred solution was slowly added 331 μL (0.498 mmol) of 1.5 M ^{t}BuLi solution via microsyringe, and the reaction mixture was warmed to room temperature and stirred for 5 min. The resulting yellow reaction mixture was filtered through Celite leaving 0.094 g (90%) of **1** as a yellow oil. ^{1}H NMR (benzene-d_6): δ = −2.21 (d, 1H, C*H*$_2$CH(CH$_3$)$_2$), −2.18 (d, 1H, C*H*$_2$CH(CH$_3$)$_2$), 0.37 (s, 9H, Si*Me*$_3$), 0.95, 0.99 (d, 6H, CH$_2$CH(C*H*$_3$)$_2$), 1.86 (s, 15H, C$_5$*Me*$_5$), 2.39 (m, 1H, CH$_2$C*H*(CH$_3$)$_2$), 5.06, 5.18, 6.10, 6.33 (m, 4H, Cp), 5.25 (s, 1H, Zr−*H*). ^{13}C NMR (benzene-d_6): δ = 0.60 (Si*Me*$_3$), 12.46 (C$_5$*Me*$_5$), 28.13 (CH$_2$CH*Me*$_2$), 29.69 (CH$_2$CH*Me*$_2$), 33.80 (CH$_2$*C*HMe$_2$), 91.32 (*C*H$_2$CHMe$_2$), 109.51, 111.80, 112.58, 113.87, 114.93 (Cp), 117.12 (*C*$_5$Me$_5$).

Preparation of Cp*Cp‴$ZrCl_2$ (3-Cl$_2$). A 250 mL round-bottomed flask was charged with 0.883 g (3.13 mmol) of $C_5H_3(SiMe_3)_3$ and 100 mL of THF. The solution was chilled in the cold well, and 2.0 mL of 1.6 M ^{n}BuLi was added dropwise via pipet. The resulting reaction mixture was warmed to room temperature and stirred for 5 h, after which time 1.319 g (3.96 mmol) of Cp*$ZrCl_3$ was added in small portions. The reaction mixture was refluxed for 3 days under Ar, and the THF was removed in vacuo. The resulting oily solid was dissolved in pentane, and the white precipitate was removed via filtration through Celite. The Celite was washed several times with fresh pentane. The solvent was removed in vacuo leaving a yellow solid, upon which recrystallization from pentane afforded 0.697 g (38%) of Cp*Cp‴$ZrCl_2$. Anal. Calcd for $Zr_1C_{24}H_{44}Cl_2Si_3$: C, 49.74; H, 7.66. Found: C, 49.41; H, 7.69. ^{1}H NMR (benzene-d_6): δ = 0.25 (s, 9H, Si*Me*$_3$), 0.45 (s, 18H, Si*Me*$_3$), 1.93 (s, 15H, C$_5$*Me*$_5$), 7.07 (s, 2H, Cp). ^{13}C NMR (benzene-d_6): δ = 1.44, 2.16 (Si*Me*$_3$), 13.29 (C$_5$*Me*$_5$), 114.94 (*C*$_5$Me$_5$), 121.45, 125.31, 126.96 (Cp).

Preparation of Cp*Cp‴Zr(CH_2CHMe_2)H (3). In the drybox, a 20 mL scintillation vial was charged with 0.105 g (0.181 mmol) of

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3-Cl$_2$ and approximately 10 mL of toluene. The clear yellow solution was frozen in the cold well. To the thawing stirred solution, 242 μL (0.363 mmol) of 1.5 M ^{t}BuLi solution was slowly added via microsyringe. The reaction mixture was warmed to room temperature and stirred for 5 min. The resulting yellow reaction mixture was filtered through Celite, and solvent was removed in vacuo leaving 0.090 g of an orange oil that is a mixture of **3** and **3a**. The resulting oil was dissolved in benzene-d_6 and placed in a J. Young NMR tube. On the vacuum line, the tube was degassed, and 1 atm of hydrogen gas was added. The tube was allowed to warm to room temperature and shaken vigorously for 5 min. After this time, the tube was reattached to the vacuum line, degassed at −196 °C, and approximately 2 equiv of isobutene was added. The tube was then thawed and shaken. ^{1}H NMR (benzene-d_6): $\delta = -2.32$ (dd, 2H, *CH*$_2$CHMe$_2$), 0.26 (s, 9H, Si*Me*$_3$), 0.37 (s, 9H, Si*Me*$_3$), 0.48 (s, 9H, Si*Me*$_3$), 1.04 (d, 3H, CH$_2$CH*Me*$_2$), 1.09 (d, 3H, CH$_2$CH*Me*$_2$), 2.01 (s, 15H, C$_5$*Me*$_5$), 2.62 (m, 1H, CH$_2$C*H*Me$_2$), 5.47 (m, 1H, Cp), 5.55 (m, 1H, Cp), 7.14 (s, 1H, Zr−*H*). ^{13}C NMR (benzene-d_6): $\delta = 1.70$ (Si*Me*$_3$), 2.63 (Si*Me*$_3$), 2.75 (Si*Me*$_3$), 13.33 (C$_5$*Me*$_5$), 28.01 (CH$_2$CH*Me*$_2$), 29.93 (CH$_2$CH*Me*$_2$), 35.17 (CH$_2$CHMe$_2$), 95.34 (*C*H$_2$CHMe$_2$), 118.24 (C$_5$*Me*$_5$), 122.16, 125.83, 128.68, 131.03, 132.22 (Cp).

Preparation of 3a. In the drybox, a 20 mL scintillation vial was charged with 0.105 g (0.181 mmol) of **3-Cl$_2$** and approximately 10 mL of toluene. The clear yellow solution was frozen in the cold well. To the thawing stirred solution was slowly added 242 μL (0.363 mmol) of 1.5 M ^{t}BuLi solution via microsyringe. The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting yellow reaction mixture was filtered through Celite, and the solvent was removed in vacuo leaving 0.076 g (83%) of a thick yellow oil. Treatment of the oil with 2 equiv of ethereal HCl provides analytically pure **3-Cl$_2$**. ^{1}H NMR (benzene-d_6): $\delta = -2.32$ (d, 1H, *CH*$_2$SiMe$_2$), −1.88 (d, 1H, *CH*$_2$SiMe$_2$), 0.24 (s, 9H, Si*Me*$_3$), 0.28 (s, 9H, Si*Me*$_3$), 0.49 (s, 3H, Si*Me*$_2$), 0.60 (s, 3H, Si*Me*$_2$), 1.98 (s, 15H, C$_5$*Me*$_5$), 6.08, 8.05 (m, 2H, Cp), 6.17 (s, 1H, Zr−*H*). ^{13}C NMR (benzene-d_6): $\delta =$ 0.74 (Si*Me*$_3$), 2.36 (Si*Me*$_3$), 3.31 (*Me*$_2$Si), 4.51 (*Me*$_2$Si), 12.96 (C$_5$*Me*$_5$), 33.62 (Me$_2$Si*C*H$_2$Zr), 119.46 (*C*$_5$Me$_5$), 111.54, 113.28, 114.94, 120.69, 131.29 (Cp).

Preparation of Cp*Cp$'''$ZrH$_2$ (6). In the drybox, a J. Young NMR tube was charged with 20 mg of **3**, and the sample was dissolved in benzene-d_6. On the vacuum line, the tube was degassed, and 1 atm of dihydrogen was admitted at −196 °C. The tube was warmed to room temperature and shaken thoroughly. ^{1}H NMR (benzene-d_6): $\delta = 0.18$ (s, 9H, Si*Me*$_3$), 0.34 (s, 18H, Si*Me*$_3$), 2.10 (s, 15H, C$_5$*Me*$_5$), 6.91 (s, 2H, Cp), 6.94 (s, 1H, Zr−*H*). ^{13}C NMR (benzene-d_6): $\delta = 1.10$ (Si*Me*$_3$), 2.28 (Si*Me*$_3$), 13.97 (C$_5$*Me*$_5$), 120.40 (*C*$_5$Me$_5$), 127.05, 127.40, 131.70 (Cp).

Preparation of Cp*$_2$Zr(CH$_2$CHMe$_2$)H (5). A 50 mL round-bottomed flask was charged with 0.560 g (1.30 mmol) of Cp*$_2$ZrCl$_2$, and approximately 25 mL of toluene was added. While the mixture was stirred at 22 °C, 1.73 mL (2.60 mmol) of 1.5 M LiCMe$_3$ in pentane was added dropwise. The reaction mixture was stirred for 10 min, filtered through a pad of Celite, and the toluene was removed in vacuo leaving 0.478 g (88%) of yellow solid identified as **5** on the basis of comparison to known spectral data.[30]

Preparation of Cp*$_2$ZrH$_2$. A 25 mL round-bottom flask was charged with 0.150 g (0.358 mmol) of **5** and 10 mL of pentane. A 180° needle valve was attached, and 1 atm of dihydrogen was admitted on the high vacuum line. The reaction mixture was stirred vigorously for 1 h, after which time the solvent was removed leaving a white solid. Recrystallization from pentane at −35 °C afforded 0.115 g (89%) of Cp*$_2$ZrH$_2$ on the basis of the known spectral data.[39]

Preparation of Cp*η^5-C$_5$H$_3$-1,3-(Si(CD$_3$)$_2$)ZrCl$_2$. In the drybox, a 50 mL round-bottom flask was charged with 650 mg (1.32 mmol) of **2** and approximately 20 mL of toluene. On the vacuum line, the flask was degassed, and 1 atm of deuterium gas was added. The reaction mixture was allowed to stir for 12 days, degassing and adding fresh deuterium daily. The reaction was monitored by ^{1}H NMR spectroscopy to demonstrate complete deuteration of the [SiMe$_3$] substituents. The reaction was then quenched by addition of 300 μL of 37% DCl in D$_2$O (w/w) via microsyringe. Upon addition, formation of a white precipitate was observed. The solvent was removed in vacuo, leaving a white solid which was then dried at 100 °C under vacuum for 12 h yielding 376 mg (56.3%) of η^5-C$_5$H$_3$-1,3-(Si(CD$_3$)$_2$)ZrCl$_2$. ^{2}H{^{1}H} NMR (toluene): $\delta = 0.35$ ppm. All other spectral features were identical to those previously reported for the protio isotopomer.

Preparation of Cp*η^5-C$_5$H$_3$-1,3-(Si(CD$_3$)$_2$)Zr(CH$_2$CDMe$_2$)(D). In the drybox, a J. Young NMR tube was charged with **2a** and dissolved in benzene-d_6. On the vacuum line, the tube was degassed, and 1 atm of deuterium was added at −78 °C. The tube was warmed to room temperature and shaken thoroughly. The reaction was monitored by ^{1}H NMR spectroscopy to demonstrate complete deuteration of the [SiMe$_3$] groups. After this, 1 equiv of isobutene was added via a calibrated gas bulb affording the desired product which was characterized by comparison with authentic samples of **2**.

Identification of Cp$''_2$Zr(CH$_2$CHMe$_2$)H (8). In the drybox, a J. Young NMR tube was charged with 26 mg (0.045 mmol) of Cp$''_2$ZrCl$_2$ and 6 mg (0.090 mmol) of solid LiCMe$_3$. On the vacuum line, the tube was degassed, and approximately 0.50 mL of toluene-d_8 was added by vacuum transfer at −78 °C. The resulting solution was maintained at −78 °C until insertion into a precooled NMR probe. ^{1}H NMR (benzene-d_6): $\delta = 0.254$ (s, 18H, Si*Me*$_3$), 0.275 (s, 18H, Si*Me*$_3$), −0.80 (m, 2H, ZrC*H*$_2$CHMe$_2$), 0.68 (d, 6.5 Hz, 3H, ZrCH$_2$CH*Me*$_2$), 2.91 (m, 1H, ZrCH$_2$C*H*Me$_2$), 4.71 (s, 1H, Zr*H*), 5.43 (m, 2H, Cp), 5.82 (m, 2H, Cp), 6.20 (m, 2H, Cp).

Preparation of [Cp$''_2$Zr]$_2$(μ_2, η^2, η^2-N$_2$) (9). In the drybox, a 250 mL round-bottom flask was charged with 0.526 g (0.906 mmol) of Cp$''_2$ZrCl$_2$ and dissolved in approximately 100 mL of toluene. The clear yellow solution was chilled in the cold well until frozen. To the thawing solution, 1.2 mL of 1.5 M ^{t}BuLi (1.8 mmol) was added. The reaction mixture was stirred for 5 min and then filtered through a pad of Celite. The toluene was removed in vacuo leaving a brown oil. Recrystallization from pentane at −35 °C affords 0.046 g (10%) of dark purple crystals identified as **5**. Anal. Calcd for Zr$_2$C$_{44}$Si$_8$H$_{84}$N$_2$: C, 50.39; H, 8.08; N, 2.67. Found: C, 49.95; H, 7.99; N, 2.48. ^{1}H NMR (benzene-d_6): $\delta = 2.30$ ppm (broad singlet, 80 Hz). Magnetic susceptibility: $\mu_{eff} = 2.73$ μB using Cp$_2$Fe as a standard in benzene-d_6.

Addition of HCl to 10. In the drybox, a 20 mL scintillation vial was charged with 27 mg (0.047 mmol) of Cp$''_2$ZrCl$_2$ and approximately 10 mL of toluene. To the stirred solution, 60 μL of 1.5 M ^{t}BuLi solution was slowly added via microsyringe. The reaction mixture was warmed to room temperature and stirred for 5 min. The resulting yellow reaction mixture was filtered through Celite, and the solvent was removed in vacuo. The resulting blue oil was dissolved in benzene-d_6 and placed in a screw cap NMR tube. Via microsyringe, 60 μL of a 2.0 M solution of HCl in diethyl ether was added resulting in immediate formation of a clear solution. Analysis by ^{1}H NMR spectroscopy reveals that Cp$''_2$ZrCl$_2$ was the sole product produced.

Addition of HCl to 8 and 10. In the drybox, a screw cap NMR tube was charged with 26 mg (0.045 mmol) of Cp$''_2$ZrCl$_2$, and a scintillation vial was charged 60 μL of 1.5 M solution of LiCMe$_3$. The pentane from the LiCMe$_3$ solution was removed in vacuo, and both the NMR tube and the vial were charged with small portions of benzene-d_6. The two solutions were combined in the NMR tube, and after about 5 min, the tube was taken outside of the drybox, and 25 μL of a 2.0 M solution of HCl in diethyl ether was added via microsyringe. Analysis of the reaction mixture by ^{1}H NMR spectroscopy revealed that Cp$''_2$ZrCl$_2$, isobutane (1 equiv), and isobutene (1 equiv) were formed as compared to authentic samples.

Addition of DCl to 8 and 10. In the drybox, a screw cap NMR tube was charged with 26 mg (0.045 mmol) of Cp$''_2$ZrCl$_2$ and approximately 0.5 mL of toluene. To the tube was added 60 μL of a

1.5 M solution of $LiCMe_3$, and after about 5 min outside of the drybox, 30 μL of 37% DCl in D_2O (w/w) was added via microsyringe. Analysis of the product by $^2H\{^1H\}$ NMR spectroscopy reveals a singlet at 0.35 ppm.

General Procedures for Kinetic Determinations. In the drybox, 0.50 mL of a 0.070 M stock solution of the zirconocene isobutyl 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 $\ln[Cp^*(CpR_n)Zr(CH_2CHMe_2)(H)]$ versus time. Activation parameters were obtained by measuring second-order rate constants over a temperature range. A plot of $\ln(k/T)$ versus $1/T$ resulted in a slope of $\Delta H^{\ddagger}/R$ and an intercept of $[(\Delta S^{\ddagger}/R) + 23.76]$.

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Supporting Information Available: Crystallographic data for **3-Cl$_2$** and **9** including complete atom labeling schemes, bond distances, and angles. Representative NMR spectroscopic and kinetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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