Carbon−Hydrogen Bond Activation with a Cyclometalated Zirconocene Hydride: Mechanistic Differences between Arene and Alkane Reductive Elimination

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Thermolysis of the cyclometalated zirconocene hydride (η^5-C_5H_3-1,3-$(SiMe_3)_2$)(η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)ZrH, at 45 °C in benzene-d_6 or toluene-d_8, resulted in H/D exchange arising from reversible C−H activation of sp^2-hybridized bonds. More careful inspection of the isotopic exchange reactions by NMR spectroscopy revealed formation of zirconocene aryl hydride complexes in equilibrium with the cyclometalated hydride compound. In contrast, activation of (dimethylamino)pyridine (DMAP) was complete at 23 °C and afforded the ortho-metalated (dimethylamino)pyridyl hydride. Performing the thermolysis of the cyclometalated zirconocene hydride in alkane solvents resulted in activation of a second [$SiMe_3$] group on the opposite cyclopentadienyl ring, forming the C_2-symmetric double-cyclometalated complex (η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)$_2$Zr. Isotopic labeling studies demonstrated that neopentane reductive elimination to yield the cyclometalated hydride proceeds through a cyclometalated assisted pathway, while the analogous extrusion of benzene occurs by direct C−H bond reductive coupling, possibly a consequence of the lower orbital reorganization energy associated with the sp^2-hybridized carbon. Activation of DMAP follows a different course, where the nucleophilicity of the heterocycle induces reductive elimination and subsequent ortho metalation. In contrast, conversion of the cyclometalated zirconocene hydride to the double-cyclometalated derivative most likely occurs by σ-bond metathesis, highlighting the various pathways available for carbon−hydrogen bond activation.

Introduction

Cyclometalated zirconocene hydride complexes are of interest, given their role in H/D exchange reactions involving saturated C−H bonds of the cyclopentadienyl substituents[1−3] and as potential conduits to low-valent zirconium species that activate small molecules such as dinitrogen.[4,5] Examples of isolable or even observable cyclometalated zirconocene hydrides are relatively rare and are typically limited to complexes containing sterically demanding silyl substituents. Mach and coworkers have reported and crystallographically characterized (η^5-$C_5Me_4SiMe_3$)(η^5-C_5Me_4-η^1-$SiMe_2CH_2$)ZrH, isolated from magnesium reduction of the corresponding zirconocene dichloride precursor.[6] Irreversible C−H activation of cyclopentadienyl substituents in zirconocene-catalyzed olefin polymerization is also believed to be an important catalyst deactivation pathway,[7,8] and the isolated cyclometalated ion-pair complex [(η^5-C_5H_2-1,2,4-$(SiMe_3)_3$)(η^5-C_5H_2-2,4-$(SiMe_3)_2$-1-η^1-$SiMe_2CH_2$)Zr][MeB(C_6F_5)$_3$] has been shown to be unreactive toward ethylene.[9]

Our laboratory has been studying the chemistry of cyclometalated zirconocene hydride complexes with the goal of using these molecules for the activation of dinitrogen, obviating the need for alkali-metal reduction procedures and offering the *potential* for catalytic N_2 functionalization.[10,11] Several examples of "mixed ring" cyclometalated hydrides have been prepared from reductive elimination of alkane (Figure 1).[4,12] Unfortunately, these complexes have shown no propensity to coordinate N_2, most likely a result of relatively electron donating cyclopentadienyl substituents that raise the activation barrier for C−H reductive elimination, prohibiting access to the desired reduced zirconium species. Introduction of purely silylated cyclopentadienyl ligands into the zirconium coordination sphere produced more facile alkane reductive elimination reactions, as extrusion of isobutane from (η^5-C_5H_3-1,3-$(SiMe_3)_2$)$_2$Zr(CH_2CHMe_2)H occurs over the course of minutes at ambient temperature to furnish the side-on-bound dinitrogen complex [(η^5-C_5H_3-1,3-$(SiMe_3)_2$)$_2$Zr]$_2$(μ_2,η^2:η^2-N_2) (Figure 1).[4] Only one diastereomer of the cyclometalated zirconocene hydride (η^5-C_5H_3-1,3-$(SiMe_3)_2$)(η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)ZrH (**1**) was identified during the alkane reductive elimination reaction.

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(1) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

(2) Chirik, P. J.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1873.

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

(4) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241.

(5) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2003**, *23*, 2797.

(6) Horacek, M.; Stepnicka, P.; Kubista, J.; Fehfarova, K.; Geypes, R.; Mach, K. *Organometallics* **2003**, *22*, 861.

(7) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(8) Bertuleit, A.; Fritze, C.; Erker, G.; Frölich, R. *Organometallics* **1997**, *16*, 2891.

(9) Choukroun, R.; Wolff, F.; Lorber, C.; Donnadieu, B. *Organometallics* **2003**, *22*, 2245.

(10) Pool, J. A.; Chirik, P. J. *Can. J. Chem.* **2005**, *83*, 286.

(11) Mori, M. J. *Organomet. Chem.* **2004**, *689*, 4210.

(12) Pool, J. A.; Bradley, C. A.; Chirik, P. J. *Organometallics* **2002**, *21*, 1271.

10.1021/om0508379 CCC: $33.50

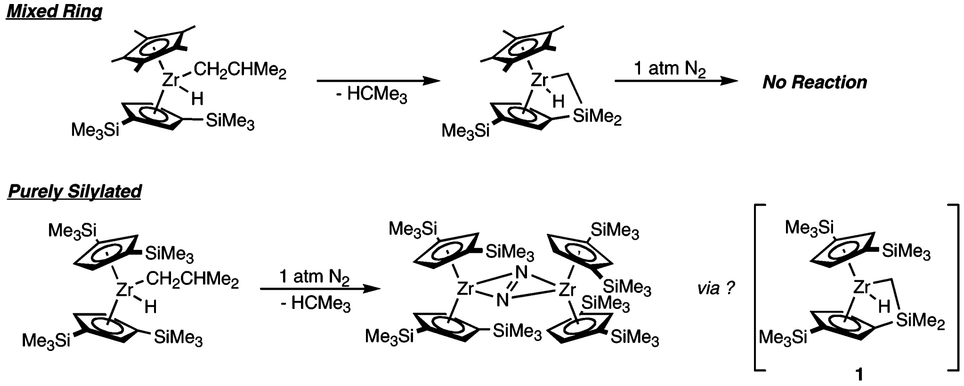
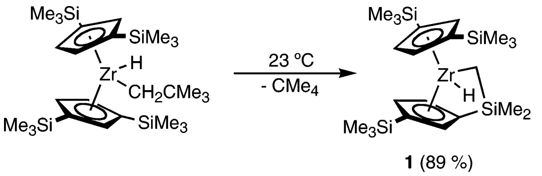


Figure 1. Cyclopentadienyl substituent effects on the reactivity of cyclometalated zirconocene hydride complexes.

On the basis of this enhanced reactivity, we became interested in developing a reliable, preparative-scale synthetic route to **1** and exploring its reactivity with traditionally robust substrates such as N_2 and alkanes. In this contribution, we report our progress toward this objective with the isolation and crystallographic characterization of **1**, along with a series of isotopic exchange and C−H activation reactions with deuterated arenes. During the course of these investigations, we have discovered that *arene* and *alkane* reductive elimination proceeds by two distinct mechanistic pathways and that the cyclometalated zirconocene hydride activates C−H bonds by a variety of different mechanisms, depending on the substrate.

Results and Discussion

Synthesis and Characterization of (η^5-C_5H_3-1,3-$(SiMe_3)_2$)(η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)ZrH (1). Previously we have reported that treatment of the zirconocene dichloride (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2ZrCl_2$ with 2 equiv of *tert*-butyllithium furnished the corresponding isobutyl hydride complex (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Zr(CH_2CHMe_2)H$, which undergoes alkane reductive elimination to afford **1**.[4] Since our initial report, we have found an improved route to **1** by reductive elimination of neopentane from (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Zr(CH_2CMe_3)H$ (eq 1).



(1)

The zirconocene alkyl hydride was readily prepared in a straightforward manner by alkylation of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$-Zr(H)Cl[12] with $LiCH_2CMe_3$. This synthetic route is preferred, as the larger neopentyl group undergoes more facile reductive elimination than does the corresponding isobutyl complex, owing to ground-state destabilization imparted by the larger alkyl ligand.[5] The isobutyl hydride route is also complicated by the need for carefully titrated *tert*-butyllithium solutions, as excess alkyllithium formed unidentified side products. Use of solid, recrystallized $LiCH_2CMe_3$ obviates these complications and, following alkane reductive elimination, reproducibly yielded pure **1**.

As we have described previously,[4] ^1H and ^{13}C NMR spectra of benzene-d_6 solutions of **1** exhibit the number of peaks consistent with formation of a single diastereomeric cyclometalated zirconocene hydride. Diagnostic doublets were observed at −4.44 and 0.62 ppm, assigned to the methylene hydrogens on the carbon bound to the zirconium. The zirconium hydride resonance appears at 5.62 ppm and has been confirmed by isotopic labeling (vide infra). We were previously unable to assign the stereochemistry of **1**, due to its propensity to undergo further chemistry (vide infra). Subsequently, we have discovered that cyclohexane-d_{12} solutions of **1** prepared under argon or vacuum are stable for extended periods.

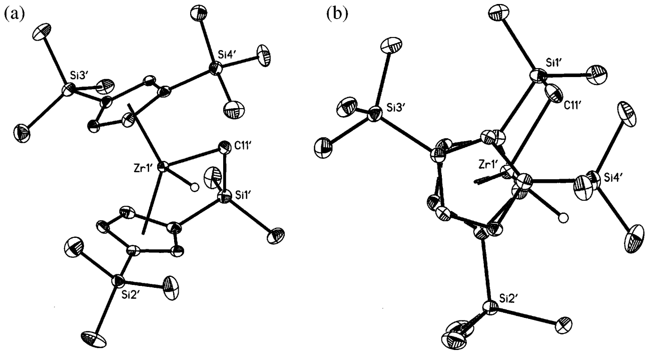


Figure 2. (a) Molecular structure of **1** shown with 30% probability ellipsoids. (b) Top view of the molecule. Hydrogen atoms, except for the zirconium hydride, are omitted for clarity.

Definitive assignment of the preferred diastereomer of **1** was accomplished by single-crystal X-ray diffraction. The compound crystallizes with two independent, enantiomeric molecules in the unit cell, one of which is presented in Figure 2. In the solid state, the two cyclopentadienyl rings are oriented in a near-gauche arrangement to avoid transannular interactions of the sterically demanding [$SiMe_3$] substituents. The intact [$SiMe_3$] group on the cyclopentadienyl ring containing the cyclometalated substituent is oriented in a lateral position with respect to the metallocene wedge, a consequence of [$SiMe_2CH_2$] coordination in the equatorial plane. This arrangement gears the [$SiMe_3$] on the opposite ring, producing the gauche conformation. The Zr(1′)−C(11′) bond length of 2.271(5) Å is in the range typically observed for zirconocene alkyls.[13] The observed diastereomer most likely arises from C−H activation of a preferred rotamer that minimizes transannular steric interactions. Previous studies on related mixed-ring derivatives allowed observation of the less favored diastereomer upon thermolysis, suggesting that reversible C−H activation proceeds with a lower barrier than rotamer interconversion.[4] While a similar energetic profile is

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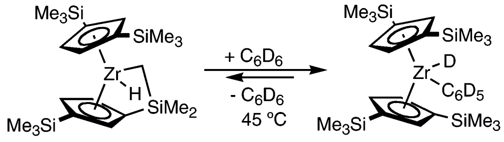
[13] For representative examples see: (a) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 637. (b) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Mayer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897. (c) Jordan, G. T.; Liu, F. C.; Shore, S. G. *Inorg. Chem.* **1997**, *36*, 5597. (d) Liu, F. C.; Liu, J.; Meyes, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293.

likely in the present case, the inability to observe other diastereomers does not exclude a Curtin−Hammett argument as the origin of the selectivity.

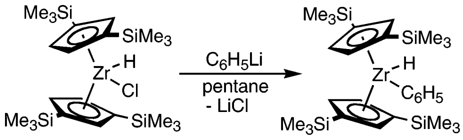
Carbon−Hydrogen Bond Activation with 1. Gently warming a benzene-d_6 solution of **1** to 45 °C over the course of 2 days and monitoring the reaction by ^{1}H NMR spectroscopy resulted in gradual disappearance of the resonances for the zirconium hydride, the cyclometalated methylene protons, and the [SiMe$_3$] groups. Removing the deuterated solvent and analyzing the resulting zirconocene by ^{2}H NMR spectroscopy in benzene confirmed deuterium incorporation into these positions, arising from H/D exchange with the NMR solvent. Careful monitoring of the isotopic exchange reaction as a function of time at 45 °C allowed observation of a new C_s-symmetric organometallic product, identified as the zirconocene phenyl-d_5 deuteride complex (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Zr(C_6D_5)D$ (**2-*d*$_6$**) (eq 2). Continued thermolysis of **1** in benzene-d_6 at 45 °C for 5 days resulted in a constant 2:1 ratio of **2-*d*$_6$** to **1-*d*$_n$**, indicating the two species are in equilibrium and C−H bond activation is reversible. Synthesis of a zirconocene phenyl hydride complex by C−H activation of benzene has been described previously, as thermolysis of the *ansa*-zirconocene dimethyl complex $Me_2Si(\eta^5\text{-}C_5Me_4)_2ZrMe_2$ under an atmosphere of H_2 at 80 °C affords $Me_2Si(\eta^5\text{-}C_5Me_4)_2Zr(C_6H_5)H$.[14]



(2)

1 **2-*d*$_6$**

Because conversion to **2-*d*$_6$** was incomplete from the thermolysis of **1** and did not exhibit its full complement of resonances due to partial deuteration, an independent synthesis of the protio isotopologue **2** was performed. Addition of 1 equiv of phenyllithium to (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Zr(H)Cl$ in pentane followed by filtration and solvent removal furnished a yellow oil identified as (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Zr(C_6H_5)H$ (**2**) on the basis of ^{1}H and ^{13}C NMR spectroscopy (eq 3). Notable features of the ^{1}H NMR spectrum of **2** are the observation of two [SiMe$_3$] environments, three cyclopentadienyl hydrogens, and a Zr−H resonance centered at 5.49 ppm. Importantly, the chemical shifts of the cyclopentadienyl and [SiMe$_3$] resonances confirm the formation of **2-*d*$_6$** from thermolysis of **1** in benzene-d_6.

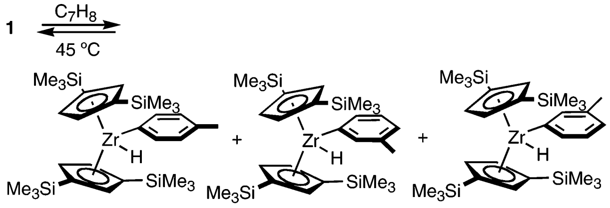


(3)

2 (81 %)

Similar isotopic exchange experiments were conducted with **1** and toluene-d_8. Thermolysis of **1** at 45 °C resulted in levels of deuterium incorporation similar to those observed with benzene-d_6 after 3 days. Examination of the ^{1}H NMR spectrum of the thermolysis reaction indicated the formation of three new zirconocene products accounting for approximately 45% of the organometallic species in solution. The remaining zirconium was **1-*d*$_n$**, again establishing an equilibrium between the cyclometalated zirconocene hydride and the corresponding aryl hydride. On the basis of ^{1}H NMR spectroscopy and degradation experiments, the three new organometallic products have been identified as isomers of the zirconocene tolyl-d_7 deuteride complex (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Zr(C_7D_7)D$ (**3-*d*$_8$**).

To identify each isomer formed and determine their relative amounts, the protio isotopologue (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Zr$-$(C_7H_7)H$ (**3**) was prepared from thermolysis of **1** in toluene and the products treated with D_2 gas. This procedure liberated free isoptopically labeled arene and formed the zirconocene dideuteride $[(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2ZrD_2]_n$ (**6-*d*$_2$**) (vide infra). Analysis of the toluene-*d* isotopomers by a combination of ^{1}H and ^{2}H NMR spectroscopy established isotopic incorporation into only the meta and para positions of the free arene. Control experiments involving addition of D_2 gas to **6-*d*$_2$** in C_7H_8 did not affect H−D exchange over the time scale of the deuteriolysis experiment. A similar degradation procedure was performed with DCl and yielded the zirconocene dichloride (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2ZrCl_2$ and the same isotopomers of toluene-*d*. In both degradation experiments, no evidence for benzylic or ortho activation of the arene was obtained. The lack of ortho activation is most likely a consequence of the steric inaccessibility of the C−H bond adjacent to the methyl group.[15] Correlating the amounts of free toluene-*d* with the ratios of the isomers of **3** observed by ^{1}H NMR spectroscopy allows tentative assignment of the major isomer as the para-activated product formed in a 7:5 ratio to the exo-meta- and endo-meta-activated products (eq 4). A 3:1 ratio of the meta products was observed; however, overlapping resonances did not allow confident assignment of the exo and endo isomers. Observation of distinct exo- and endo-meta isomers indicates restricted rotation about the zirconium−aryl bond.

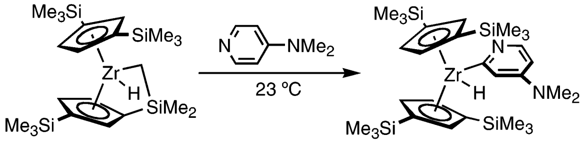


(4)

3-*para* **3-*endo-meta*** **3-*exo-meta***

major

Carbon−hydrogen activation was also explored with heterocycles. Addition of 1 equiv of (dimethylamino)pyridine (DMAP) to **1** resulted in ortho metalation over the course of 8 h at 23 °C to afford a single isomer of **4** (eq 5). Identification of the regiochemistry of the C−H-activated product was accomplished by treatment of **4** with deuterium chloride, yielding (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2ZrCl_2$ and DMAP-*d* with deuterium exclusively in the ortho position of the arene. Unfortunately, definitive assignment of the stereochemistry, namely exo versus endo selectivity, was not accomplished, due to poor resolution of the coordinated DMAP resonances that are key for structural elucidation by two-dimensional NMR experiments. For simplicity, the exo isomer (relative to the pyridine nitrogen) is depicted



(5)

1 **4** (51 %)

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(14) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255.

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

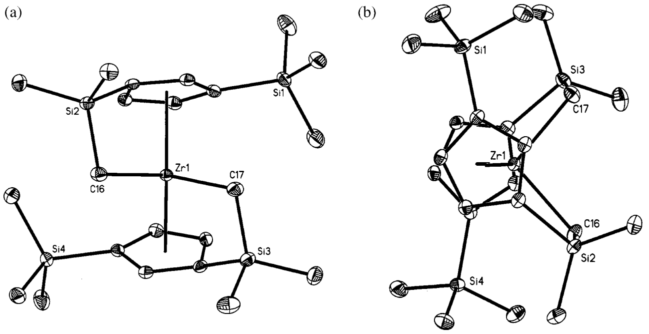
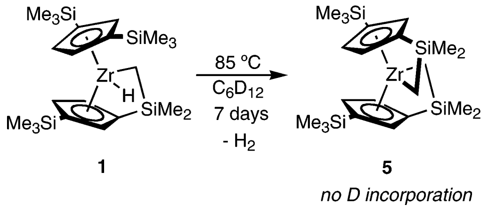


Figure 3. (a) Molecular structure of **5** shown with 30% probability ellipsoids. (b) Top view of the molecule. Hydrogen atoms are omitted for clarity.

in eq 5 on the basis of literature precedent with cationic zirconocene complexes[16] and a related neutral bis(indenyl)zirconium derivative, which has been structurally characterized.[17]

Thermolysis in Alkane Solvents. The facile isotopic exchange observed with **1** and deuterated arenes prompted further exploration of the scope of the C−H bond activation reaction. Of particular interest was the reactivity of **1** with saturated alkanes. Thermolysis of **1** in cyclohexane-d_{12} at 85 °C for several days did not result in isotopic exchange into the zirconium hydride, the methylene hydrogens, or the [$SiMe_3$] substituents, suggesting that productive, reversible oxidative addition of the sp^3−hybridized C−D bonds of the solvent was not operative. Performing the thermolysis on a preparative scale for 1 week in heptane solution afforded a yellow solid identified as one isomer of the double-cyclometalated zirconocene (η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)$_2$Zr (**5**) (eq 6).



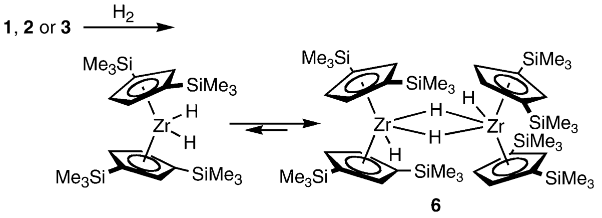
(6)

1 **5**

no D incorporation

The ^{1}H NMR spectrum of **5** in cyclohexane-d_{12} or benzene-d_6 exhibits the number of resonances consistent with a C_2-symmetric compound, indicating that the second C−H activation occurs on the cyclopentadienyl ring opposite the first. Two diagnostic doublets with coupling constants of 14 Hz were observed upfield of $SiMe_4$ at −2.37 and −1.40 ppm for the diastereotopic methylene hydrogens on the carbon bound to zirconium. A single zirconium methylene resonance was also observed at 16.9 ppm by ^{13}C NMR spectroscopy. Confirmation of the assignment of the observed isomer was provided by X-ray diffraction. The solid-state structure of **5** (Figure 3) contains nearly idealized C_2 molecular symmetry and confirms cyclometalation of the [$SiMe_3$] substituents from the opposite cyclopentadienyl ring. The Zr(1)−C(16) and Zr(1)−C(17) bond distances are statistically invariant at 2.320(2) and 2.316(2) Å and are slightly elongated from the lengths typically encountered for zirconocene alkyls.[13] Similar observations have been made by Mach and co-workers, where thermolysis of a cyclometalated zirconocene hydride yielded a double-cyclometalated zirconocene where activation of the second silyl group occurred on the ring opposite of the first.[6]

Synthesis and Characterization of [(η^5-C_5H_3-1,3-($SiMe_3$)$_2$)$_2ZrH_2$]$_n$. During the process of identifying the product ratio arising from toluene activation, D_2 gas was added to the mixture of **1** and the isomers of **3**, liberating toluene-*d*. Concomitant with this process is the formation of a white powder identified as the zirconocene dideuteride [(η^5-C_5H_3-1,3-($SiMe_3$)$_2$)$_2ZrD_2$]$_n$ (**6-d_2**). This compound is sparingly soluble in aromatic hydrocarbons and is essentially insoluble in pentane. Moreover, the protio isotopologue **6** can be prepared from H_2 addition to pure **1**, **2**, or **3** (eq 7). The ^{1}H NMR spectrum of **6** recorded in benzene-d_6 exhibits the number of peaks for two compounds. The major resonances correspond to a molecule with a C_s-symmetric ligand environment that also exhibits distinct peaks for bridging and terminal zirconium hydrides centered at −3.57 and 3.41 ppm, respectively.[2] Additional signals for a minor C_{2v}-symmetric compound were also observed, tentatively assigned as the ziroconocene dihydride monomer. Quantitation of the amount of monomer versus dimer in solution could not be reliably accomplished, due to the partial solubility of **6** in benzene-d_6.

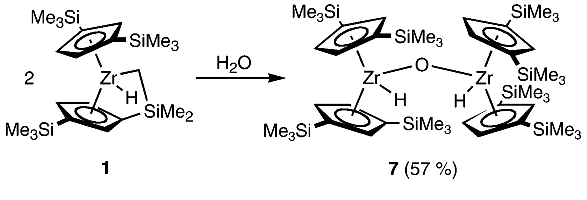


(7)

6

Formation of relatively robust hydride bridges in **6** are in contrast with the monomeric, *tert*-butyl-substituted congener (η^5-C_5H_3-1,3-(CMe_3)$_2$)$_2ZrH_2$.[2] The difference in position of the monomer−dimer equilibrium between the two zirconocene dihydrides is most likely a result of cooperative steric and electronic effects. The metal center in **6** is less hindered compared to that in (η^5-C_5H_3-1,3-(CMe_3)$_2$)$_2ZrH_2$, owing to longer C−Si bonds relative to C−C bonds with the purely alkyl substituents. Likewise, studies from our laboratory[4] and others[18] have shown the silyl-substituted cyclopentadienyl ligands impart more electrophilic metal centers compared to their alkylated counterparts. Taken together, these effects support the formation of significant quantities of coordinatively saturated zirconocene dihydride dimers.

Both **1** and **6** are extremely sensitive molecules. The presence of even trace amounts of water with either compound cleanly afforded the zirconocene μ-hydride complex [(η^5-C_5H_3-1,3-($SiMe_3$)$_2$)$_2$ZrH]$_2$(μ_2-O) (**7**) (eq 8). Colorless blocks suitable for X-ray diffraction were isolated from cooling a concentrated pentane solution to −35 °C. The solid-state structure is presented in Figure 4, and the data were of sufficient quality such that all of the hydrogens in the molecule were located and refined. Two data sets were collected on two independently prepared samples and produced identical results. An idealized C_2 molecular



(8)

1 **7** (57 %)

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(16) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546.

(17) Bradley, C. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 8110.

(18) 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.; Kiester, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525.

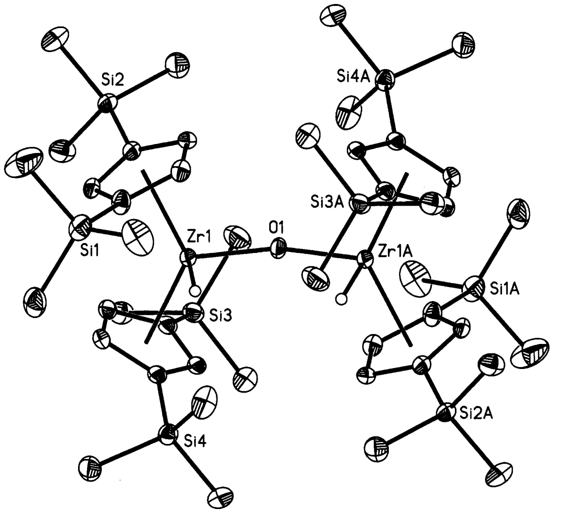


Figure 4. Molecular structure of **7** shown with 30% probability ellipsoids. Hydrogen atoms, except for the zirconium hydride, are omitted for clarity. The oxygen atom and the zirconium hydrides are disordered over two positions; only one is shown.

geometry with a transoid orientation of the zirconium hydrides is observed. The structure possesses half occupancy of both the oxygen and hydride atoms. The Zr−H and Zr−O distances of 1.88(5) and 1.931(3) Å, respectively, are in good agreement with those previously reported for zirconium hydride and oxo compounds.[19] The bent Zr−O−Zr bond (bond angle 153.05(17)°) is unusual, as typically linear linkages of this type are observed. Examples of bent Zr−O−Zr bonds have been reported in several different μ-oxo zirconocenes.[20]

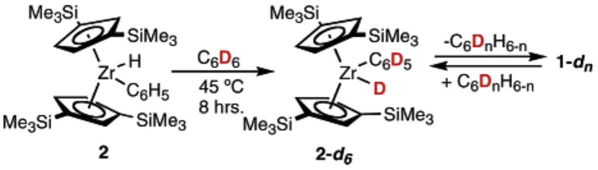
Another notable feature of the solid-state structure is the coplanarity of the two zirconocene fragments. An orthogonal orientation of the two metallocene cores would be expected if Zr−O π-bonding was dominant. However, previous work from our laboratory with zirconocenes[4] and from Evans with lanthanides[21] has established that this specific (bis)cyclopentadienyl prefers coplanarity in the solid state of dimeric structures. The solution NMR data collected on the same batch of crystals used for the diffraction experiment were also consistent with a dimeric structure with coplanar zirconocene fragments, as C_s rather than C_1 symmetry was observed.

Isotopic Labeling Studies and Mechanistic Considerations. A series of isotopic labeling experiments were conducted in order to gain insight into the mechanism of H/D exchange and arene C−H bond activation. Because it is well-established that zirconocene dihydrides promote H/D exchange,[1,2] isotopic substitution during the preparation of **6** from **1** was initially studied. One atmosphere of D_2 gas was added to a thawing benzene solution of **1** and the ^2H NMR spectrum immediately recorded. Formation of **6-*d*$_n$** was instantaneous at ambient temperature, and deuterium incorporation was observed in the bridging and terminal deuteride positions as well as in the [SiMe$_3$] groups of the cyclopentadienyl ligands (eq 9). These results do not distinguish between direct deuteriolysis of the Zr−CH_2 linkage or reductive elimination of the cyclometalated zirconocene hydride to form a transient sandwich compound that undergoes D_2 oxidative addition followed by reversible cyclometalation. By way of comparison, the double-cyclometalated zirconocene **5** is resistant toward hydrogenation (deuteration), requiring heating to 65 °C for 2 days for conversion to **6**.

(9)

* denotes D incorporation

Isolation of the zirconocene phenyl hydride complex **2** allowed the study of isotopic exchange in aryl hydride complexes. Thermolysis of **2** at 45 °C over the course of 8 h in benzene-d_6 resulted in disappearance of the phenyl resonances between 6.98 and 7.19 ppm along with the zirconium hydride centered at 5.49 ppm. A combination of ^1H and ^2H NMR spectroscopy revealed clean conversion to **2-*d*$_6$** before any **1** could be detected (eq 10). Significantly, the disappearance of the phenyl and zirconium hydride resonances occurred at the same rate and only trace amounts of deuterium incorporation into the [SiMe$_3$] groups were observed during the transformation. At longer reaction times, the equilibrium between isotopologues of **2-*d*$_n$** and **1-*d*$_n$** was established and additional isotopic exchange into the [SiMe$_3$] groups was observed.



(10)

Formation of the isotopologue of **2-*d*$_6$** with an equal proportion of Zr−D and Zr−Ph-d_5 was unexpected, on the basis of the previously proposed mechanism for alkane reductive elimination from zirconocene alkyl hydride complexes.[1,4,5] An example of this pathway is presented in Figure 5 and proceeds through initial metal-to-ring hydrogen transfer followed by oxidative addition of a C−H bond. This could either be intramolecular, arising from a cyclopentadienyl substituent, or intermolecular, derived from addition of an external C−H bond from arene solvent. Reductive elimination of alkane then occurs followed by hydrogen migration to yield the observed product. Regardless of whether the C−H activation event is intra- or intermolecular, the starting zirconium hydride (the deuteride is illustrated in Figure 5 for clarity) remains in the complex and is not transferred to the alkane. Thus, if this mechanism were operative for the isotopic exchange with **2** and benzene-d_6, the expected product is *not* **2-*d*$_6$** but rather its isotopologue, (η^5-C_5H_3-1,3-(SiMe$_3$)$_2$)$_2$Zr(C_6D_5)H (**2-*d*$_5$**).

To further probe if cyclometalated-assisted reductive elimination was operative with this specific zirconocene aryl hydride complex, the zirconocene phenyl deuteride (η^5-C_5H_3-1,3-(SiMe$_3$)$_2$)$_2$Zr(C_6H_5)D (**2-*d***) was prepared from (η^5-C_5H_3-1,3-(SiMe$_3$)$_2$)$_2$Zr(D)Cl and phenyllithium. Thermolysis of a pentane solution of **2-*d*** at 45 °C for 10 h and monitoring of the reaction

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(19) Crystallographically characterized hydrides: (a) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 821. (b) Stones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889. (c) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973. Zirconium oxo: (d) Reid, A. F.; Shannon, J. S.; Swan, J. M.; Wailes, P. C. *Aust. J. Chem.* **1965**, *18*, 173. (e) Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2267. (f) Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179.

(20) For representative examples see: (a) Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr., Sect. B* **1974**, *30*, 2267. (b) Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179. (c) Koyama, M.; Kimura, K.; Nakano, M.; Yamazaki, H. *Chem. Lett.* **1998**, 1139. (d) Green, J. C.; Green, M. L. H.; Taylor, G. C.; Saunders: J. *Dalton Trans.* **2000**, 317.

(21) Evans, W. J.; Allen, N. T.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 359.

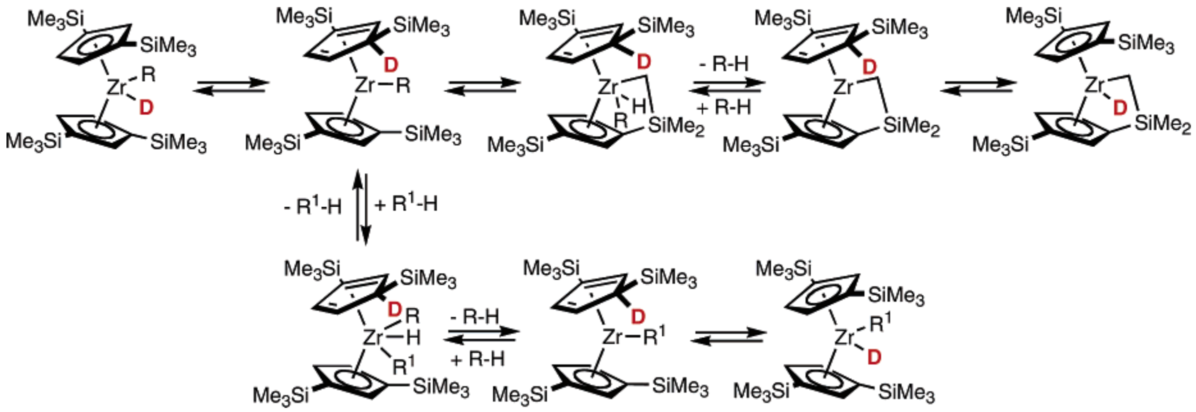
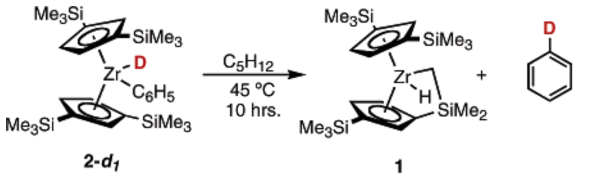


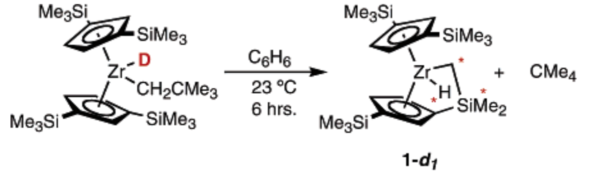
Figure 5. Cyclometalated-assisted pathway for alkane reductive elimination from zirconocene alkyl hydride complexes.

by ^{2}H and ^{1}H NMR spectroscopy revealed formation of benzene-*d* along with **1** (eq 11). Importantly, no deuterium incorporation was observed in **1**, clearly demonstrating *direct* benzene reductive elimination from **2-*d***.



(11)

Because the results of benzene reductive elimination from **2-*d*** contrast with the cyclometalated-assisted pathway previously reported for *isobutane* reductive elimination from both $(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CHMe_2)H$[1] and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)Zr(CH_2CHMe_2)H$,[4] the mechanism of neopentane extrusion from $(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2Zr(CH_2CMe_3)D$ was examined. Alkylation of $(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2Zr(D)Cl$ with $LiCH_2CMe_3$ at 23 °C furnished $(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2Zr(CH_2CMe_3)D$. Allowing the zirconocene neopentyl deuteride to stand at ambient temperature for 3 h resulted in clean conversion to **1-*d*** with loss of neopentane (eq 12). Examination of the products by ^{2}H and ^{1}H NMR spectroscopy revealed formation of isotopomers of **1-*d*$_1$** with deuterium in the zirconium hydride, zirconium methylene, and the [SiMe$_3$] substituents. The poor resolution of ^{2}H NMR spectroscopy did not allow definitive assignment of the [SiMe$_3$] groups that were deuterated and did not show if other diastereomers of **1** were accessed during the reductive elimination reaction. Significantly, no deuterium incorporation into the free alkane was observed, clearly supporting cyclometalated-assisted reductive elimination for neopentane formation.



* denotes D incorporation

(12)

One question raised by these results is as follows: why does the mechanism of reductive elimination change depending on whether alkyl or aryl substituents are coordinated in the zirconocene wedge? The lower orbital reorganizational energy associated with C−H bond formation from an sp^2 aryl ligand most likely makes the direct reductive elimination pathway energetically accessible.[22] In the case of sp^3 alkyl group C−H bond reductive coupling,[15,23] the more directional orbital raises the barrier for direct reductive elimination and the cyclometalated-assisted pathway becomes competitive.

While direct C−H bond formation was observed for arene reductive coupling, this mechanism does not account for the experimentally observed isotopic exchange with **1**. A competing pathway must account for deuterium incorporation into the zirconium hydride, methylene, and [SiMe$_3$] groups. Two alternative mechanisms seem plausible. The first (Figure 6, path A) is a σ-bond metathesis pathway,[24] involving exchange of an arene C−D bond with the zirconium methylene. Subsequent benzene-d_5 reductive elimination followed by reversible oxidative addition and reductive elimination sequences involving isotopomers and isotopologs of **1-*d*$_n$** would account for the experimental observation of deuterium in the Zr−*H*, Zr−C*H*$_2$, and [SiMe$_3$] positions. The major limitation of this mechanism is that it contradicts established σ-bond metathesis preferences, whereby metal hydrides are known to undergo metathesis more rapidly than more directional sp^3-hybridized metal−alkyl bonds.[24] An alternative σ-bond metathesis mechanism with the zirconium hydride is also possible, liberating HD gas, which then hydrogenates the zirconium−aryl or −alkyl bond (Figure 6). Only productive pathways to account for deuterium incorporation into the cyclopentadienyl ligand are illustrated in Figure 6.

The second possibility is a reversible oxidative addition−reductive elimination sequence (Figure 6, path B). For observable H−D exchange to occur, this pathway must occur by a cyclometalated-assisted mechanism, allowing deuterium from the free arene to incorporate into the zirconocene product. While direct C−H reductive coupling for **2-*d*** and **2** occurs with a lower barrier than the cyclometalated-assisted alternative, the observation of deuterium scrambling *after* isotopic exchange of **2** with benzene-d_6 suggests that a higher barrier cyclometalated-assisted pathway may indeed be accessible at longer reaction times.

The conversion of **1** to the double-cyclometalated zirconocene **5** provided some insight into the barrier for σ-bond metathesis. Recall that this reaction takes place over the course of 1 week at 85 °C, in comparison to the isotopic exchange reactions,

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[22] (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613. (b) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727. (c) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 6928. (d) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 8321. (e) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482.

[23] (a) Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403. (b) Janak K. E.; Churchill, D. G.; Parkin, G. *Chem. Commun.* **2003**, 22.

[24] 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.

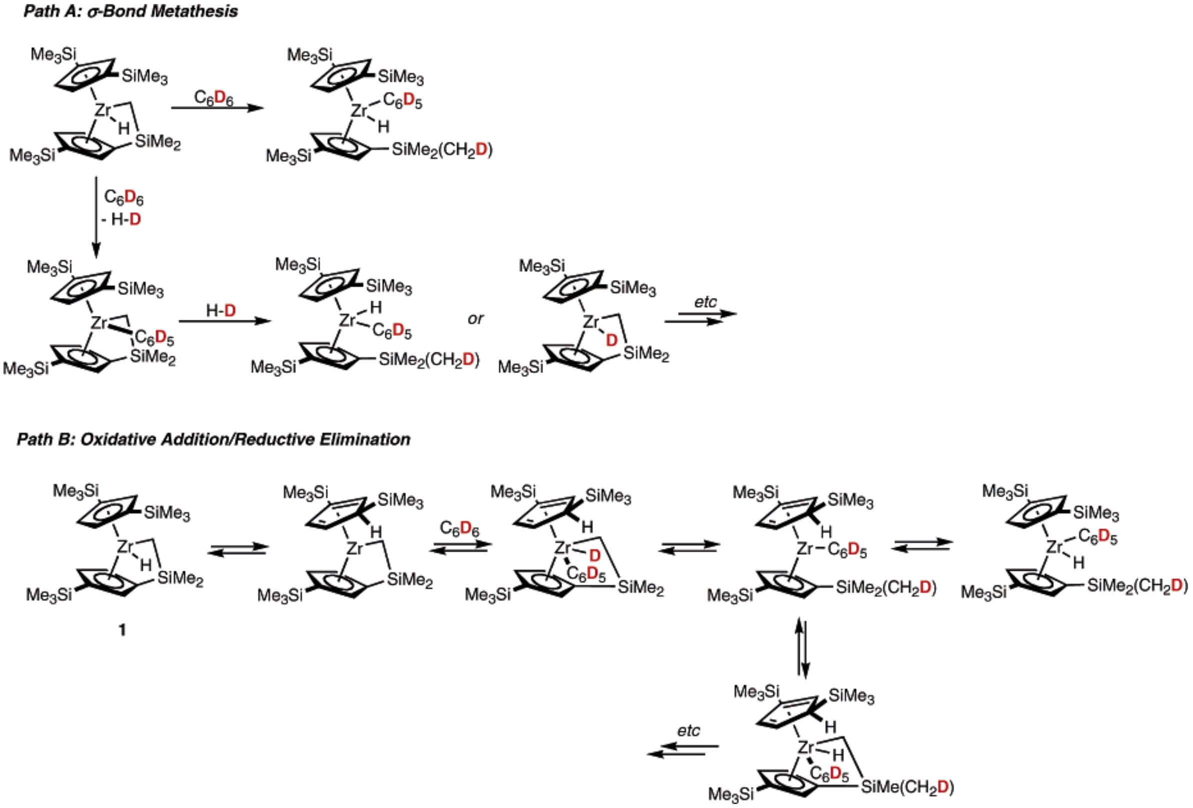
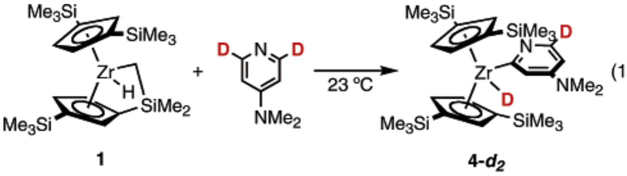


Figure 6. Possible mechanisms for isotopic exchange with **1** and benzene-d_6.

which occur in hours at 45 °C. In addition, hydrogenation of **5** to yield **1** and ultimately **6** is slow, requiring 2 days at 65 °C. To further probe the possibility of σ-bond metathesis, the zirconocene phenyl hydride complex **2** was exposed to deuterium gas at 23 °C. The deuteration to **6-d_n** was slow, requiring 2 days to reach completion. Significantly, no deteurium was incorporated into to either the Zr−*H* or Zr−*Ph* positions prior to conversion to the zirconocene deuteride product. While not conclusive evidence, taken together, these results suggest that σ-bond metathesis pathways with these molecules occur with relatively high barriers, supporting cyclometalated-assisted reductive elimination−oxidative addition sequences as the mechanism for H−D exchange.

The mechanism of ortho C−H activation of DMAP was also explored. Addition of 1 equiv of 4-(dimethylamino)pyridine-2,6-d_2 (DMAP-d_2)[25] to **1** furnished **4-d_2** with deuterium located only in the ortho pyridyl position and the zirconium deuteride (eq 13). As with the isotopic exchange between **2** and benzene-d_6, these results are inconsistent with a cyclometalated-assisted pathway. In addition, no deuterium incorporation was observed in the [SiMe$_3$] substituents, ruling out a σ-bond metathesis pathway involving the arene and zirconium methylene. While the alternate σ-bond metathesis mechanism involving reaction of Zr−H with the heterocycle liberating H−D cannot be definitively excluded, we believe this process is unlikely, as a completely isotopically selective capture of the intermediate zirconocene aryl cyclometalate with H−D must be invoked. More plausible is a ligand-induced reductive elimination pathway, initially observed in zirconocene chemistry by Schwartz and co-workers,[26] whereby the DMAP nitrogen coordinates to **1** and induces direct C−H bond reductive coupling and dissociation.[27]



(13)

Concluding Remarks

A reliable synthetic route to a crystallographically characterized, yet reactive, cyclometalated zirconocene hydride has been devised. Isotopic exchange with arene solvents such as benzene-d_6 and toluene-d_8 occurred over the course of hours at 45 °C and proceeds through observable zirconocene aryl hydride (deuteride) complexes. More careful examination of the mechanism of reductive elimination revealed that reductive coupling with zirconocene aryl substituents occurred through a direct C−H bond-forming process, while the analogous reaction with zirconocene alkyls proceeds through a cyclometalated-assisted pathway. The lower orbital reorganization energy in the former case is believed to account for the observed mechanistic preferences. However, it is postulated that a cyclometalated-assisted pathway competes with the direct process and is responsible for isotopic exchange. Carbon−hydrogen bond activation of more nucleophilic heterocyclic substrates such as (dimethylamino)pyridine occurs through a ligand-induced reductive elimination pathway. Conversion of **1** to **5** most likely occurs by σ-bond metathesis, highlighting the variety of mechanistic pathways available to the cyclometalated zirconocene hydride for C−H bond activation.

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[25] Rubottom, G. M.; Evain, E. J. *Tetrahedron* **1990**, *46*, 5055.

[26] (a) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246. (b) Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *162*, C11. (c) Yoshifuji, M.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *153*, C15.

[27] We are unable to distinguish between this pathway and one involving reversible reductive elimination and oxidative addition of the cyclometalated hydride, forming a transient bis(cyclopentadienyl)zirconium sandwich which then oxidatively adds the sp^2-hybridized ortho C−H bond.

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.[28] Toluene, benzene, pentane, and heptane were further dried by distillation from "titanocene".[29] Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Benzene-d_6 and toluene-d_8 were further dried by storage and distillation from "titanocene" immediately before use. Argon and hydrogen gas were purchased from Airgas Inc. and passed through a column containing manganese oxide on vermiculite and 4 Å molecular sieves before admission to the high-vacuum line. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz (^1H) and 100.511 MHz (^{13}C). All chemical shifts are reported relative to $SiMe_4$ using ^1H (residual) or ^{13}C NMR chemical shifts of the solvent as a secondary standard. (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(H)Cl,[4] $LiCH_2CMe_3$[30] and DMAP-d_2[25] were prepared as described previously. The zirconocene deuterio chloride (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(D)Cl was prepared in a manner analogous to that for the hydride isotopomer using $KBEt_3D$.[31]

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 ($\lambda = 0.710\,73$ 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.

Spectroscopic Identification of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(CH_2CMe_3)H. A flame-dried 100 mL round-bottom flask was charged with 0.963 g (1.77 mmol) of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(H)Cl and 0.137 g (1.77 mmol) of neopentyllithium. The flask was attached to a swivel frit apparatus and removed from the drybox. On the vacuum line, pentane was added by vacuum transfer at −78 °C. The resulting reaction mixture was stirred under argon for 30 min, after which time the white precipitate was removed by filtration and washed with cold pentane. The solvent was removed in vacuo, yielding a yellow oil identified as (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(CH_2CMe_3)H. ^1H NMR (benzene-d_6): δ 0.18 (s, 2H, CH_2CMe_3), 0.31 (s, 18H, $SiMe_3$), 0.33 (s, 18H, $SiMe_3$), 1.12 (s, 9H, CH_2CMe_3), 5.47 (m, 1H, Cp), 6.20 (m, 1H, Cp), 6.67 (m, 1H, Cp), 5.77 (s, 1H, Zr−*H*). $^{13}C\{^1H\}$ NMR (cyclohexane-d_{12}): δ 1.65, 1.71 ($SiMe_3$), 26.64 (CMe_3), 114.13, 115.84, 117.74, 119.86, 120.11 (Cp).

Preparation of (η^5-C_5H_3-1,3-$(SiMe_3)_2$)(η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2$)ZrH (1). A flame-dried 25 mL round-bottom flask was charged with 0.301 g (0.551 mmol) of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(H)Cl and 0.043 g (0.551 mmol) of neopentyllithium and attached to a 180° needle valve. The assembly was removed from the drybox, and approximately 10 mL of pentane was added by vacuum transfer at −78 °C. The resulting reaction mixture was warmed to room temperature and stirred overnight under vacuum. Following filtration, the solvent was removed in vacuo to yield 0.255 g (89%) of a yellow oil identified as **1**. Analytically pure material can be obtained in lower yields by recrystallization of concentrated pentane solutions at −35 °C. Anal. Calcd for $C_{22}H_{42}ZrSi_4$: C, 51.80; H, 8.30. Found: C, 51.66; H, 7.94. ^1H NMR (benzene-d_6): δ −4.44 (d, 13 Hz, 1H, CH_2SiMe_3), 0.62 (d, 13 Hz, 1H, CH_2SiMe_3), 0.18 (s, 9H, $SiMe_3$), 0.22 (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$), 0.37 (s, 3H, $SiMe_2$), 0.44 (s, 3H, $SiMe_2$), 5.34 (m, 1H, Cp), 5.60 (m, 1H, Cp), 6.16 (m, 1H, Cp), 6.21 (m, 1H, Cp), 6.98 (m, 1H, Cp), 7.49 (m, 1H, Cp), 5.62 (s, 1H, Zr−*H*). $^{13}C\{^1H\}$ NMR (cyclohexane-d_{12}): δ −0.067, 0.37, 0.40, 0.83, 1.53 (Si*Me*), 36.11 ($ZrCH_2SiMe_2$), 112.74, 113.39, 114.68, 115.99, 117.02, 122.03, 122.13, 126.02, 126.87, 130.21 (Cp).

Preparation of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(C_6H_5)H (2). A 20 mL scintillation vial was charged with 0.120 g (0.220 mmol) of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(H)Cl, 122 μL of 1.8 M PhLi (0.220 mmol) in cyclohexane/diethyl ether, and approximately 10 mL of pentane. The resulting solution was stirred for 16 h, turning pale yellow over time. The mixture was filtered through Celite and the solvent removed in vacuo to yield 0.105 g (81%) of a yellow oil identified as **2**. ^1H NMR (benzene-d_6): δ 0.09 (s, 18H, $SiMe_3$), 0.23 (s, 18H, $SiMe_3$), 5.49 (s, 1H, Zr−*H*), 6.00 (m, 2H, Cp), 6.41 (m, 1H, Cp), 6.98−7.19 (Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 0.35, 0.61 ($SiMe_3$), 113.20, 114.12, 122.82, 123.28, 125.25, 125.99, 127.16, 127.68, 128.20 (Cp/Ph).

Spectroscopic Identification of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(η^1-C_6H_5Me)H (3). A flame-dried 50 mL round-bottom flask was charged with 0.347 g (0.636 mmol) of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(H)Cl, 0.050 g (0.640 mmol) of $LiCH_2CMe_3$, and 25 mL of toluene, and a 180° needle valve was attached. The resulting reaction mixture was stirred at 45 °C for 4 days. Aliquots of the solution were taken, and the progress of the reaction was monitored periodically by ^1H NMR spectroscopy. Analysis showed a mixture of **1** and three isomers of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(η^1-C_6H_5Me)H. ^1H NMR (benzene-d_6): major isomer (**3**-*para*), 0.08 (s, 18H, $SiMe_3$), 0.26 (s, 18H, $SiMe_3$), 2.26 (s, 3H, C_6H_5Me), 5.28 (s, 1H, Zr−*H*), 6.02 (m, 2H, Cp), 6.42 (m, 1H, Cp), 6.82−7.12 (C_6H_5Me); minor isomers (**3**-*meta*), 0.09 (s, 18H, $SiMe_3$), 0.14 (s, 18H, $SiMe_3$), 0.23 (s, 18H, $SiMe_3$), 0.27 (s, 18H, $SiMe_3$), 2.12 (s, 3H, C_6H_5Me), 2.20 (s, 3H, C_6H_5Me), 5.25 (s, 1H, Zr−*H*), 5.28 (s, 1H, Zr−*H*), 5.50 (m, 1H, Cp), 6.00 (m, 1H, Cp), 6.04 (m, 1H, Cp), 6.12 (m, 1H, Cp), 6.45 (m, 1H, Cp), 6.51 (m, 1H, Cp), 6.82−7.12 (C_6H_5Me).

Preparation of (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2$Zr(2-NC_5H_3-4-NMe_2)H (4). A 20 mL scintillation vial was charged with 0.111 g (0.218 mmol) of **1**, 0.031 g (0.250 mmol) of 4-(dimethylamino)pyridine, and 15 mL of diethyl ether. The reaction mixture was stirred for 16 h, turning pale yellow. The solvent was removed in vacuo and the residue extracted with pentane. Chilling the concentrated solution to −35 °C overnight yielded 0.069 g (51%) of faint brown crystals identified as **4**. Anal. Calcd for $C_{29}H_{52}ZrSi_4N_2$: C, 55.09; H, 8.29; N, 4.43. Found: C, 54.90; H, 8.20; N, 4.05. ^1H NMR (benzene-d_6): δ 0.22 (s, 18H, $SiMe_3$), 0.40 (s, 18H, $SiMe_3$), 2.37 (s, 6H, NMe_2), 3.78 (s, 1H, Zr−*H*), 5.79 (m, 1H, Cp), 5.99 (m, 2H, Cp), 5.97 (m, 1H, *py*), 7.20 (m, 1H, *py*), 7.89 (m, 1H, *py*). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 1.09, 1.38 ($SiMe_3$), 39.34 (NMe_2), 108.5, 111.6, 115.9, 117.4, 119.5 (Cp), 109.3, 114.3, 147.8, 154.5, 193.8 (py).

Preparation of (η^5-C_5H_3-3-$SiMe_3$-1-η^1-$SiMe_2CH_2)_2$Zr (5). A thick-walled flame-dried reaction vessel was charged with 0.038 g (0.075 mmol) of **1**. On a high-vacuum line, the contents of the vessel were degassed and approximately 5 mL of heptane was added by vacuum transfer at −78 °C. The resulting reaction mixture was then heated to 85 °C for 1 week. After this time, the solvent was removed in vacuo to give an oily solid. This yielded yellow blocks of **5** following recrystallization from pentane at −35 °C. Anal. Calcd for $C_{22}H_{40}ZrSi_4$: C, 52.00; H, 7.93. Found: C, 52.19; H, 8.26. ^1H

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(28) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(29) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 203.

(30) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

(31) Klusener, P. A. A.; Brandsma, L.; Verkruijsse, H. D.; Schleyer, P. v. R.; Friedl, T.; Pi, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 465.

NMR (cyclohexane-d_{12}): δ −2.37 (d, 2H, 14 Hz, C*H*$_2$SiMe$_3$), −1.40 (d, 2H, 14 Hz, C*H*$_2$SiMe$_3$), 0.19 (s, 18H, Si*Me*$_3$), 0.25 (s, 6H, Si*Me*$_2$), 0.29 (s, 6H, Si*Me*$_2$), 5.73 (m, 2H, Cp), 5.93 (m, 2H, Cp), 6.93 (m, 2H, Cp). ^{13}C{^{1}H} NMR (cyclohexane-d_{12}): δ −0.85, 0.30, 0.41, 1.73 (Si*Me*), 16.9 (Zr*C*H$_2$), 110.8, 116.5, 118.1, 118.8, 127.4 (Cp).

Preparation of [(η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$)$_2$ZrH$_2$]$_2$ (6). A thick-walled reaction vessel was charged with 0.151 g (0.297 mmol) of **1** and approximately 10 mL of pentane. On a high-vacuum line, the vessel was submerged in liquid nitrogen and evacuated and 4 atm of dihydrogen was admitted. The contents of the vessel were warmed to ambient temperature, and the resulting reation mixture was stirred for 16 h. The excess H$_2$ was removed in vacuo and the precipitate collected by filtration, yielding 0.077 g (51%) of a white powder identified as **6**. Anal. Calcd for $C_{44}H_{88}Zr_2Si_8$: C, 51.59; H, 8.66. Found: C, 51.57; H, 8.27. ^{1}H NMR (benzene-d_6): δ −3.57 (br, 2H, Zr−*H*), 0.23 (s, 36H, Si*Me*$_3$), 0.51 (s, 36H, Si*Me*$_3$), 3.41 (br, 2H, Zr−*H*), 5.05 (br, 4H, Cp), 6.08 (br, 4H, Cp), 6.59 (br, 4H, Cp). ^{13}C{^{1}H} NMR (benzene-d_6): δ −0.33, 1.69 (Si*Me*$_3$), 114.05, 117.75, 120.14 (Cp). **(**η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$)$_2$ZrH$_2$: ^{1}H NMR (benzene-d_6) δ 0.58 (s, 36H, Si*Me*$_3$), 5.91 (m, 4H, Cp), 7.80 (m, 2H, Cp), Zr−*H* not located; ^{13}C{^{1}H} NMR (benzene-d_6) δ 2.22 (Si*Me*$_3$), 119.80, 122.56 (Cp). *Quaternary carbons were not located in either case*.

Preparation of [(η^5-C$_5$H$_3$-1,3-(SiMe$_3$)$_2$)$_2$ZrH]$_2$(μ_2-O) (7). A 25 mL round-bottom flask was charged with 0.150 g (0.295 mmol) of **1** and approximately 10 mL of diethyl ether and attached to a 180° needle valve. Against an Ar counterflow, 6 μL of distilled water was added to the yellow solution via microsyringe. The resulting reaction mixture was stirred at ambient temperature for 30 min. The solvent was removed in vacuo and the residue washed with cold pentane, yielding 0.087 g (57%) of an off-white powder identified as **7**. Anal. Calcd for $C_{44}H_{86}Zr_2Si_8$: C, 50.90; H, 8.35. Found: C, 50.22; H, 7.97. ^{1}H NMR (benzene-d_6): δ 0.47 (s, 36H, Si*Me*$_3$), 0.48 (s, 36H, Si*Me*$_3$), 5.18 (s, 2H, Zr−*H*), 5.58 (m, 4H, Cp), 5.89 (m, 4H, Cp), 6.53 (m, 4H, Cp). ^{13}C{^{1}H} NMR (benzene-d_6): δ 2.04, 2.11 (Si*Me*$_3$), 118.16, 120.27, 120.51, 120.88, 125.28 (Cp).

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Supporting Information Available: A figure giving a representative ^{1}H NMR spectrum of **2** in benzene-d_6 and CIF files giving crystallographic data for **1**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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