Organometallics **2002,** *21,* 1271−1277 1271

A Convenient Method for the Synthesis of Zirconocene Hydrido Chloride, Isobutyl Hydride, and Dihydride Complexes Using *tert*-Butyl Lithium

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Received December 27, 2001

Preparation of zirconocene hydrido chloride complexes has been accomplished via addition of 1 equiv of *tert*-butyllithium to the corresponding zirconocene dichlorides. In this manner, both $Cp^*Cp''Zr(H)Cl$ and $Cp''_2Zr(H)Cl$ ($Cp^* = C_5Me_5$, $Cp'' = 1,3\text{-}(SiMe_3)_2C_5H_3$) were prepared in high yield. Further addition of ^tBuLi to $Cp^*Cp''Zr(H)Cl$ affords the isobutyl hydride complex $Cp^*Cp''Zr(CH_2CHMe_2)(H)$, which upon addition of 1 atm of dihydrogen undergoes rapid hydrogenolysis yielding the monomeric dihydride $Cp^*Cp''ZrH_2$. In the absence of dihydrogen, the zirconocene dihydride undergoes reversible C−H activation of a cyclopentadienyl trimethylsilyl group, affording the "tuck-in" derivative $Cp^*(\eta^5\text{-}1\text{-}SiMe_3C_5H_3\text{-}3\text{-}(\eta^1\text{-}SiMe_2CH_2))ZrH$. Addition of 2 equiv of ^tBuLi to the *ansa*-zirconocene $^iPr_2Si(\eta^5\text{-}3\text{-}SiMe_3C_5H_3)(\eta^5\text{-}3,4\text{-}(SiMe_3)_2C_5H_2)ZrCl_2$ results in the corresponding zirconocene isobutyl hydride complex, which upon exposure to H_2 affords the dimeric dihydride $[^iPr_2Si(\eta^5\text{-}3\text{-}SiMe_3C_5H_3)(\eta^5\text{-}3,4\text{-}(SiMe_3)_2C_5H_2)ZrH_2]_2$. In a similar procedure the substituted indenyl complexes *rac*-$(1\text{-}CMe_3{-}C_9H_6)Zr(H)Cl$ and *rac*-$(1\text{-}CMe_3{-}C_9H_6)Zr(CH_2CHMe_2)(H)$ have been prepared. This synthetic methodology allows for the preparation of metallocene alkyl hydrides and dihydrides inaccessible by more traditional routes.

Introduction

The rich chemistry of group IV metallocene alkyl and hydride complexes has elevated this interesting class of molecules to the forefront of organotransition metal chemistry. Catalytic applications such as olefin[1] and imine hydrogenation,[2] stereospecific olefin polymerization,[3] and stoichiometric transformations such as hydrozirconation[4] and dinitrogen activation[5] have been, in part, responsible for this considerable interest. Traditionally, the synthesis of group 4 metallocene hydride complexes has relied on hydrogenation of the corresponding metallocene dimethyl complexes,[6] often at elevated pressure[7] and temperature.[8] Alternative procedures such as reaction of the metallocene dichlorides with borohydride and aluminohydride reagents have proven moderately sucessful.[9,10] Once prepared, the dihydride complexes may serve as synthons for a variety of metallocene alkyl derivatives.[11]

In principle, β-hydrogen elimination from a zirconocene alkyl followed by loss of free olefin provides another pathway to zirconocene hydride complexes (eq 1).[12] Although isotopic labeling studies have shown the reaction to be kinetically facile,[4c] judicious choice of the alkyl is essential, as in most cases β-hydrogen elimination followed by olefin dissociation is thermodynamically unfavorable.[13] Alkyls such as *tert*-butyl are attractive candidates for this purpose due to the paucity of stable early transition metal *tert*-butyl complexes.[14] For example, addition of 1 equiv of ^tBuLi to zirconocene dichloride provides $Cp_2Zr(CH_2CHMe_2)Cl$ instead of the corresponding *tert*-butyl compound.[15] Addition of a second equivalent of ^tBuLi at low temperature allows for spectroscopic identification of the zirconocene dialkyl

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(1) (a) Troutman, M. V.; Appella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4916. (b) Broene, R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 5, 12569. (c) Waymouth, R. M.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911.

(2) (a) Ringwald, M.; Sturmer, R.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1999**, *121*, 1524. (b) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703. (c) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952.

(3) (a) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (b) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13. (c) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(4) (a) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115. (b) Wipf, P.; Takahashi, H.; Zhuang, N. *Pure Appl. Chem.* **1998** *70*, 1077. (c) Chirik, P. J. Day, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 10308.

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

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

(7) Couturier, S.; Gautheron, B. *J. Organomet. Chem.* **1978**, *157*, C61.

(8) (a) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

(9) (a) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2289. (b) Larsonneur, A.; Choukroun, R.; Jaud, J. *Organometallics* **1993**, *12*, 3216. (c) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

(10) Buchwald, S. L.; LaMaire, S. J.; Nielson, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

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

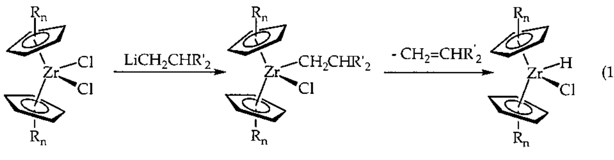
(12) This pathway has been implicated in numerous catalytic cycles involving zirconocene alkyls, the most prominent being olefin polymerization. For more information see ref 3.

(13) For a recent example of stable zirconocene dialkyls containing β-hydrogens see: Wendt, O. F.; Bercaw, J. E. *Organometallics* **2001**, *20*, 3891.

(14) Bougeard, P.; McCullough, J. J.; Sayer, B. G.; McGlinchey, M. J. *Inorg. Chim. Acta* **1984**, *89*, 133.

10.1021/om011090z CCC: $22.00
Publication on Web 02/21/2002

$Cp_2Zr(CMe_3)(CH_2CHMe_2)$, which upon warming above −60 °C provides a source of $[Cp_2Zr]$.[16]



Herein we describe a convenient and straightforward method for the synthesis of zirconocene hydrido chloride, isobutyl hydride, and in some cases, dihydride complexes, from the metallocene dichlorides using commercially available *tert*-butyllithium. This route has proven to be a reliable, high-yield synthetic procedure that allows access to zirconocene complexes unavailable via conventional synthetic pathways. During the course of our investigations, we have obtained the solid-state structures for a new *ansa*-zirconocene dichloride as well as two zirconocene hydrido chloride complexes.

Results and Discussion

Addition of 1 equiv of ^tBuLi (1.5 M solution in pentane) to a thawing toluene solution of $Cp^*Cp''ZrCl_2$ (**1**, $Cp'' = \eta^5$-1,3-$(SiMe_3)_2C_5H_3$) followed by filtration to remove LiCl afforded $Cp^*Cp''Zr(H)Cl$ (**2**) as a yellow solid in 85% yield. Using a similar procedure, the preparation of $Cp''_2Zr(H)Cl$ (**3**) was also achieved.[17] In both cases, inequivalent trimethylsilyl and cyclopentadienyl resonances are observed in the ^1H and ^{13}C NMR spectra. In benzene-d_6, downfield Zr-*H* resonances are observed at 6.22 and 6.33 ppm for **2** and **3**, respectively, which are similar to those reported for $Cp^*_2Zr(H)Cl$ (6.59 ppm) and $Cp^*CpZr(H)Cl$ (6.90 ppm).[18]

Chilling concentrated pentane solutions of **2** to −35 °C deposits yellow blocks suitable for X-ray diffraction. As shown in Figure 1, **2** is monomeric in the solid state. The trimethylsilyl substituents on the cyclopentadienyl ring are oriented to avoid congestion in the narrow ("back") portion of the metallocene, thus providing ample steric protection to prevent dimerization through hydride bridges. The diffraction data were of sufficient quality such that each hydrogen atom, including the zirconium hydride, could be located and refined isotropically. The experimentally determined zirconium hydride distance of 1.78(2) Å is in accord with other crystallographically characterized zirconium hydrogen bonds.[19]

Monitoring the reaction between **1** and solid ^tBuLi in situ by ^1H NMR spectroscopy in benzene-d_6 demonstrates rapid conversion to **2** along with formation of 1 equiv of free isobutene. Isobutane and hexamethylethane, the signature organic byproducts for the disproportionation and recombination of *tert*-butyl radicals,[20] were not detected. Observation of free olefin is consistent with formation of an intermediate zirconocene *tert*-butyl chloride compound[15] that undergoes β-hydrogen elimination, resulting in the hydrido chloride product, **2** (eq 2). Although we currently favor a β-hydrogen elimination/olefin dissociation pathway,[15b] hydride transfer from *tert*-butyllithium to the zirconocene via short-lived or caged radical intermediates cannot be excluded.

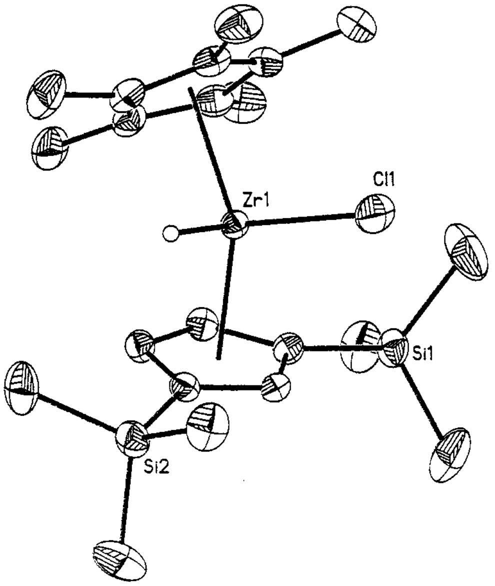
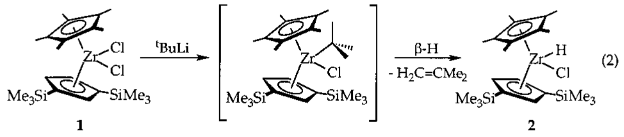


Figure 1. Molecular structure of $Cp^*Cp''Zr(H)Cl$ (**2**) (50% probability ellipsoids; hydrogen atoms omitted for clarity).



Reaction of **2** with an additional equivalent of ^tBuLi or addition of 2 equiv of ^tBuLi to **1** at low temperature affords the zirconocene isobutyl hydride complex $Cp^*Cp''Zr(CH_2CHMe_2)(H)$ (**4**) in near quantitative yield. Isolation of the isobutyl hydride rather than the dihydride demonstrates the increased reactivity of the punitive zirconocene dihydride toward isobutylene as compared to the hydride chloride **2**. Addition of 1 atm of dihydrogen to **4** results in formation of the zirconocene dihydride $Cp^*Cp''ZrH_2$ (**5**), along with 1 equiv of isobutane (Scheme 1). In benzene-d_6, the ^1H NMR spectrum of **5** displays a broad singlet at 6.89 ppm for the zirconium hydride, consistent with a monomeric dihydride.[6] This resonance broadens into the baseline upon addition of 1 atm of dihydrogen, indicative of rapid exchange between the zirconium dihydride and free H_2.

Over the course of 1 h in the absence of dihydrogen, **5** readily converts to the "tuck-in" derivative $Cp^*(\eta^5$-1-$SiMe_3$,-C_5H_3-3-$(\eta^1$-3-$SiMe_2CH_2))ZrH$ (**6**) (Scheme 1). Formation of **6** is reversible; exposure to 1 atm of dihydrogen rapidly regenerates **5**. Addition of deuterium gas to related metallocene dihydrides such as $Cp^*(\eta^5$-C_5H_3-1,3-$(CMe_3)_2)ZrH_2$ results in deuteration of the *tert*-butyl

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[15] (a) Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825. (b) Barr, K. J.; Watson, B. T.; Buchwald, S. L. *Tetrahedron Lett.* **1991**, *32*, 5465.

[16] Negishi, E.; Takahshi, T. *Acc. Chem. Res.* **1994**, *27*, 124.

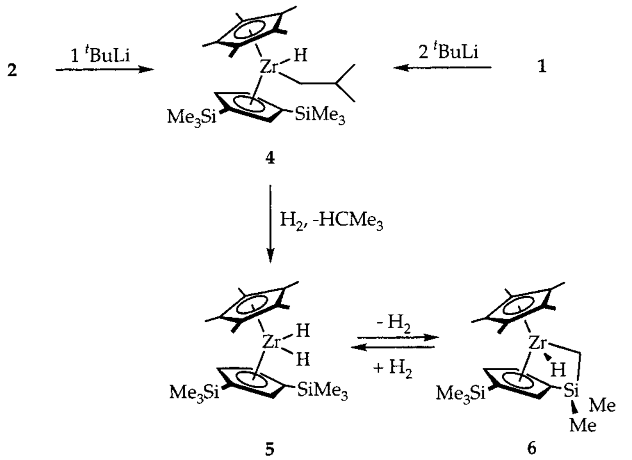
[17] Preparation of **3** is best accomplished under an atmosphere of argon and in relatively dilute (~0.02 M) toluene solutions. Performing the reaction in more concentrated solutions and under an atmosphere of N_2 affords a dinitrogen complex. Pool, J. A.; Chirik, P. J. Manuscript in preparation.

[18] Woo, H.-G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198.

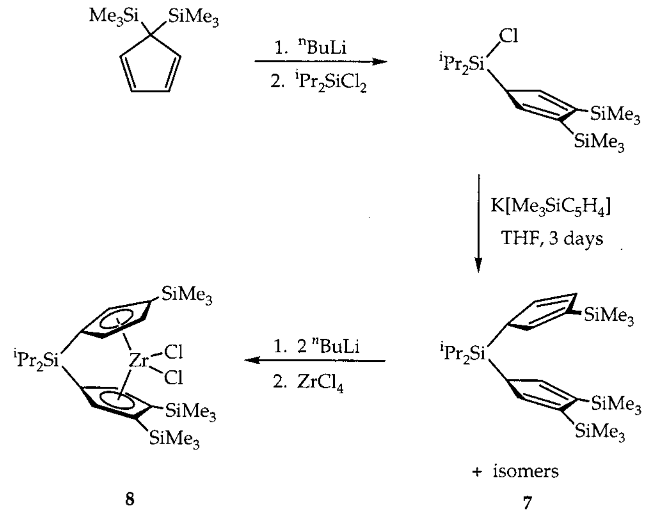
[19] Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973.

[20] (a) Weydert, M.; Brennan, J. G.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1995**, *14*, 3942. (b) Terry, J. O.; Futrell, J. H. *Can. J. Chem.* **1968**, *46*, 664.

Scheme 1



Scheme 2



groups on the cyclopentadienyl ring, implicating the formation of tuck-in intermediates.[6] Incorporation of an isotopic label into the Cp* ligands has not been observed, suggesting that the two *tert*-butyl substituents constrain the Cp* ligand in an orientation unsuited to methyl group metalation.[6] In the present case, the longer Si−C bonds of the trimethylsilyl groups favor the formation of an observable tuck-in complex.

Extension of this synthetic methodology to *ansa* metallocene systems was also of interest, owing to the observation that in the presence of dinitrogen $\{rac\text{-}Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2\}ZrH_2$ undergoes facile thermal reductive elimination of dihydrogen and formation of a side-on coordinated dinitrogen complex.[5] The utility of this transformation has been limited by the tedious and low-yield synthesis associated with preparation of the zirconocene dichloride precursor $\{rac\text{-}Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2\}ZrCl_2$.[21] The optimized synthetic procedure requires refluxing the dipotassio salt of the *ansa*-dicyclopentadienide ligand with $ZrCl_4$ in toluene for one month, resulting in only 15% yield of the desired zirconocene dichloride.

With the goal of preparing a monomeric *ansa*-metallocene dihydride having an improved metalation procedure, a new silylene-bridged ligand was designed. The target zirconocene contains sterically demanding substituents in the 3- and 4-positions of the cyclopentadiene rings to prevent hydride dimerization, while the 2- and 5-positions adjacent to the linking group are occupied by hydrogens. This reduces the steric bulk in the narrow portion of the wedge, thereby expediting formation of the *ansa*-zirconocene. Since the direct synthesis of 1,2-dialkyl-substituted cyclopentadienes is often tedious,[22] we opted for the preparation of silylated cyclopentadienes to exploit facile silyl and hydrogen migrations, which may provide the desired regiochemistry.[23] Linking bis-trimethylsilyl cyclopentadienes with a standard dimethylsilylene bridge yields metallocenes as a mixture of regio- and stereochemical isomers.[24] Incorporation of larger isopropyl substituents on the silylene fragment favors the isomer in which the trimethylsilyl groups avoid unfavorable steric interactions with the linking moiety, affording a cyclopentadienyl with adjacent silyl substituents.[25] This feature also eliminates complications arising from the possibility of *racemo* and *meso* isomers.

The synthesis of ${}^iPr_2Si(3,4\text{-}(SiMe_3)_2C_5H_3)(3\text{-}SiMe_3C_5H_4)$ (**7**) commenced with the addition of ${}^iPr_2SiCl_2$ to a chilled THF solution of LiCp″, resulting in ${}^iPr_2Si(3,4\text{-}(SiMe_3)_2C_5H_3)Cl$ in high yield (Scheme 2).[25] Attempts to prepare ${}^iPr_2Si(3,4\text{-}(SiMe_3)_2C_5H_3)_2$ by refluxing ${}^iPr_2Si(3,4\text{-}(SiMe_3)_2C_5H_3)Cl$ with an excess of LiCp″ or KCp″[26] in THF produced no reaction. Displacement of the chloride was accomplished by refluxing ${}^iPr_2Si(3,4\text{-}(SiMe_3)_2C_5H_3)Cl$ with $K[C_5H_4SiMe_3]$,[24] affording **7** as a mixture of double bond isomers in 93% yield. Characterization of **7** was achieved through a combination of NMR spectroscopy and mass spectrometry.

The desired zirconocene dichloride, ${}^iPr_2Si(\eta^5\text{-}3,4\text{-}(SiMe_3)_2C_5H_2)(\eta^5\text{-}3\text{-}SiMe_3C_5H_3)ZrCl_2$ (**8**), was prepared via in situ deprotonation of **7** in THF followed by addition of $ZrCl_4$ and heating to reflux for 3 days. Recrystallization from pentane yields **8** as an air-stable, orange solid in 40% isolated yield. The synthesis (not optimized) of **8** occurs on a much shorter time scale (3 days versus 1 month) than that described for $\{rac\text{-}Me_2Si(\eta^5\text{-}C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2\}ZrCl_2$ and in significantly higher yield. Slow evaporation of a concentrated pentane solution of **8** afforded yellow-orange plates suitable for X-ray diffraction. The solid-state structure of **8**, shown in Figure 2, displays a typical coordination environment for an *ansa*-zirconocene dichloride. The crystal structure also confirms the identity of **8** and establishes the desired regiochemistry of the trimethylsilyl subsitutuents.

Addition of 2 equiv of ${}^tBuLi$ to a thawing toluene solution of **8** resulted in the clean formation of $\{{}^iPr_2Si(\eta^5\text{-}3\text{-}SiMe_3C_5H_3)(\eta^5\text{-}3,4\text{-}(SiMe_3)_2C_5H_2)\}Zr(CH_2CHMe_2)(H)$ (**9**) in high yield (eq 3). Although two isomers of the alkyl hydride are plausibile, only one (>95%) is observed by NMR spectroscopy. The identity of the preferred

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(21) Chacon, S. T.; Coughlin, E. B.; Henling, L. M.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *497*, 171.

(22) Hughes, R. P.; Kowalski, A. S.; Lomprey, J. R.; Neithamer, D. R. *J. Org. Chem.* **1996**, *61*, 401.

(23) Jutzi, P. *Chem. Rev.* **1986**, *86*, 983.

(24) Ihara, E.; Yoshoika, S.; Furo, M.; Katsura, K.; Yasuda, H.; Mohri, S.; Kanehisa, N.; Kai, Y. *Organometallics* **2001**, *20*, 1752.

(25) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988.

(26) Edelman, M. A.; Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Tian, S. *J. Organomet. Chem.* **1998**, *550*, 397.

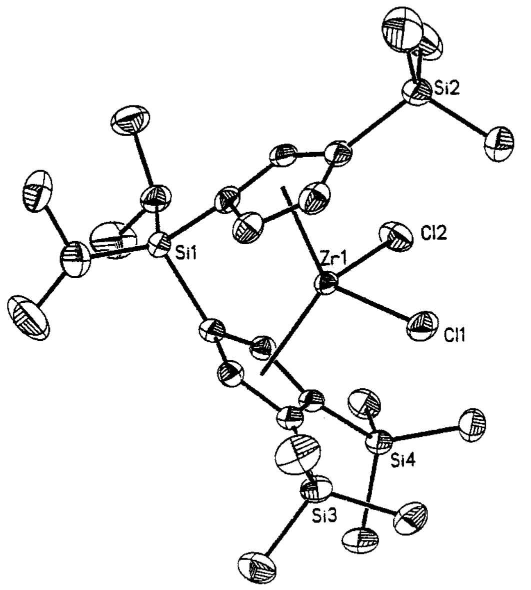
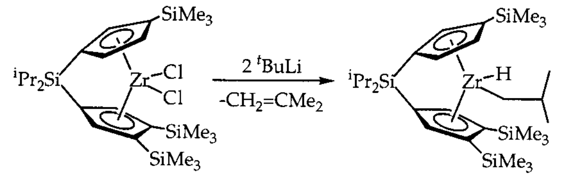


Figure 2. Molecular structure of ${}^{i}Pr_2Si(\eta^5\text{-}3,4\text{-}(SiMe_3)_2\text{-}C_5H_2)(\eta^5\text{-}3\text{-}SiMe_3C_5H_3)ZrCl_2$ (**8**) (50% probability ellipsoids; hydrogen atoms omitted for clarity).

isomer has been established by NOESY NMR spectroscopy. The observed alkyl hydride is the one in which the isobutyl ligand is coordinated to avoid unfavorable steric interactions with the trimethylsilyl group of the monosubstituted (excluding the linker) cyclopentadienyl ring. Hydrogenolysis of **9** proceeded rapidly with 1 atm of dihydrogen at 25 °C, resulting in the dimeric zirconocene dihydride $[{}^{i}Pr_2Si(\eta^5\text{-}3\text{-}SiMe_3C_5H_3)(\eta^5\text{-}3,4\text{-}(SiMe_3)_2\text{-}C_5H_2)ZrH_2]_2$ (**10**), with liberation of 1 equiv of isobutane.[27]



8 **9** (3)

Synthesis of indenyl-substituted zirconcene hydrido chloride, isobutyl hydride, and dihydride complexes was also investigated. Addition of 1 equiv of ${}^{t}BuLi$ to a yellow toluene slurry of *rac*-$(1\text{-}CMe_3C_9H_6)_2ZrCl_2$[28] (**11**) followed by filtration resulted, quite unexpectedly, in formation of the isobutyl hydride complex *rac*-$(1\text{-}CMe_3C_9H_6)Zr(CH_2\text{-}CHMe_2)(H)$ (**13**), whereas the desired hydrido chloride complex *rac*-$(1\text{-}CMe_3C_9H_6)Zr(H)Cl$ (**12**) was observed only in trace (<10%) quantities (eq 4). The low solubility of **11** in hydrocarbon solvents accounts for these observations. Once formed, the increased solubility of **12** results in a facile reaction with the relatively high concentration of ${}^{t}BuLi$ in the reaction mixture, affording **13** as the predominant product. Separation of excess **11** has been achieved by filtration of the reaction mixture through a pad of Celite. A more efficient and practical synthesis of **13** may be achieved via addition of 2 equiv of ${}^{t}BuLi$ to **11**.

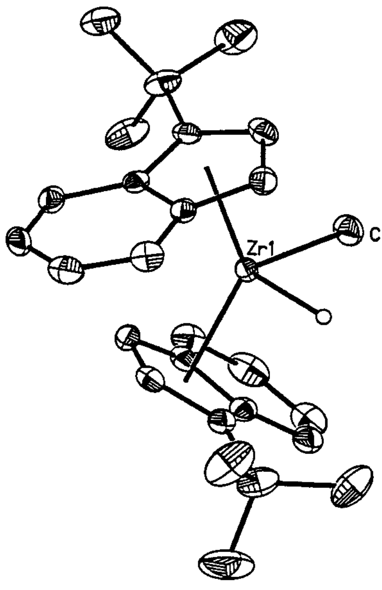
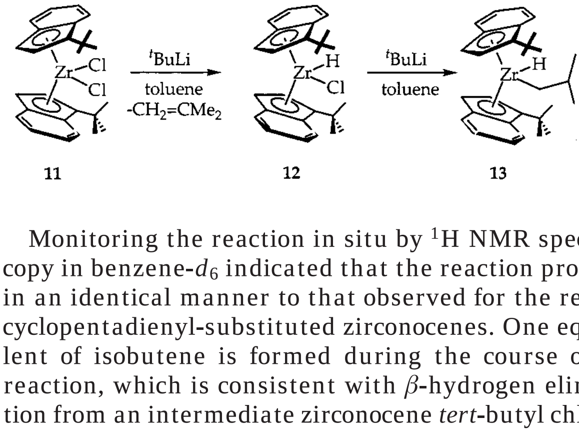


Figure 3. Molecular structure of *rac*-$(1\text{-}CMe_3\text{-}C_9H_6)Zr(H)\text{-}Cl$ (**12**) (50% probability ellipsoids; hydrogen atoms omitted for clarity).



11 **12** **13** (4)

Monitoring the reaction in situ by ${}^{1}H$ NMR spectroscopy in benzene-d_6 indicated that the reaction proceeds in an identical manner to that observed for the related cyclopentadienyl-substituted zirconocenes. One equivalent of isobutene is formed during the course of the reaction, which is consistent with β-hydrogen elimination from an intermediate zirconocene *tert*-butyl chloride complex. Addition of 1 atm of dihydrogen to **13** at 25 °C results in immediate formation of 1 equiv of isobutane and no tractable amount of the zirconocene dihydride.

Isolation of **12** in pure form has been achieved via addition of 1 equiv of $NaBEtH_3$ to a chilled toluene solution of **11**. Filtration of the reaction mixture followed by recrystallization from toluene affords yellow-green crystals of **12** (eq 5). In benzene-d_6 solution, **12** displays a singlet at 4.56 ppm assigned to the zirconium hydride resonance. The solid-state structure (Figure 3) of **12** has been elucidated by single-crystal X-ray diffraction and confirms the identity of the *racemo* isomer. Retention of stereochemistry upon addition of ${}^{t}BuLi$ to **11** is significant since previous studies have shown *racemo*–*meso* interconversions of zirconocene complexes are induced by addition of alkyllithium reagents.[6,29] The solid-state structure also confirms the monomeric nature of **11**, demonstrating the ability of the *tert*-butyl indenyl ligand to provide sufficient steric protection to preclude dimerization through formation of hydride

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[27] The dimeric zirconocene dihydride appears to be unstable. Allowing benzene-d_6 solutions of **10** to stand under ambient conditions results in significant decomposition over the course of 1 h.

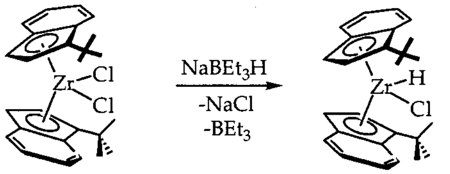
[28] Grimmer, N. E.; Coville, N. J.; de Koning, C. B.; Smith, J. M.; Cook, L. M. *J. Organomet. Chem.* **2000**, *616*, 112.

[29] Lee, L. W. M.; Piers W. E.; Parvez M.; Rettig S. J.; Young V. G. *Organometallics* **1999**, *19*, 3904.

Table 1. Crystal Data and Structure Refinements for 2, 8, and 12

	2	**8**	**12**
empirical formula	$C_{21}H_{37}Cl_1Si_2Zr$	C_{25} H_{46} Cl_2 Si_4 Zr	C_{26} H_{31} Cl Zr
fw	472.36	621.10	470.18
space group	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
unit cell dimens	$a = 11.2731(3)$ Å	$a = 11.4889(3)$ Å	$a = 8.7779(5)$ Å
	$b = 15.9450(4)$ Å	$b = 20.0585(4)$ Å	$b = 18.6034(10)$ Å
	$c = 14.9885(3)$ Å	$c = 15.0962(2)$ Å	$c = 14.3166(7)$ Å
	$\beta = 111.896(2)°$	$\beta = 107.302(2)°$	$\beta = 107.409(2)°$
volume	2499.82(10) Å^3	3321.50(12) Å^3	2230.8(2) Å^3
Z	4	4	4
density(calcd)	1.255 Mg/m^3	1.242 Mg/m^3	1.400 Mg/m^3
abs coeff	0.645 mm^{-1}	0.648 mm^{-1}	0.622 mm^{-1}
$F(000)$	992	1304	976
cryst size	0.30 × 0.30 × 0.15 mm^3	0.40 × 0.30 × 0.05 mm^3	0.15 × 0.10 × 0.05 mm^3
θ range for data collection	2.33−32.09°	2.03−32.23°	2.65−26.37°
index ranges	$-14 < h < 14, -23 < k < 21, -21 < l < 21$	$-16 < h < 15, -26 < k < 29, -22 < l < 22$	$-10 < h < 8, -22 < k < 23, -17 < l < 16$
no. of reflns collected	21 742	30 303	11 178
no. of ind reflns	6901 [R(int) = 0.0243]	9707 [R(int) = 0.0386]	4529 [R(int) = 0.0430]
completeness to $\theta = 32.09°$	78.9%	82.5%	99.5%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	6901/0/374	9707/0/425	4529/0/377
goodness-of-fit on F^2	0.983	1.022	1.007
final R indices [$I>2\sigma(I)$]	R1 = 0.0271, wR2 = 0.0686	R1 = 0.0500, wR2 = 0.1257	R1 = 0.0426, wR2 = 0.0866
R indices (all data)	R1 = 0.0349, wR2 = 0.0722	R1 = 0.0683, wR2 = 0.1351	R1 = 0.0635, wR2 = 0.0936
largest diff peak and hole	0.416 and −0.400 e Å^{-3}	1.568 and −1.034 e Å^{-3}	0.474 and −0.550 e Å^{-3}

bridges.[30] The crystal structure was of sufficient quality such that all hydrogen atoms on the indenyl and *tert*-butyl fragments, as well as the zirconium hydride, could be located in the Fourier difference map and freely refined. A Zr−H distance of 1.86(3) Å was determined from the diffraction experiment and is in accord with other structurally characterized zirconium hydrides (vide infra).



(5)

The methodology described herein offers a convenient and straightfoward synthetic protocol for the preparation of a range of zirconocene hydrido chloride, isobutyl hydride, and dihydride complexes. In addition to its simplicity, the procedure is advantageous since, in many cases, access to the dihydride compounds described is unachieveable using conventional hydrogenolysis or reduction methods.[31]

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, and cannula techniques or in an M. Braun drybox under an atmosphere of prepurified nitrogen or argon as described previously.[32] 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.[33] Deuterated solvents for NMR spectroscopy were degassed using three freeze−pump−thaw cycles and stored over 4 Å molecular sieves. Hydrogen gas was purchased from Airgas Incorporated and passed through a trap of liquid nitrogen immediately before use. Preparation of Cp''_2ZrCl_2,[34] $C_5H_4(SiMe_3)_2$, KCp″, $K[Me_3SiC_5H_4]$,[26] $^iPr_2Si(3,4\text{-}(SiMe_3)_2C_5H_3)Cl$,[25] and **11**[28] were accomplished as described previously. Cp^*ZrCl_3 was purchased from Strem Chemical Company, 1.5 M ^{t}BuLi solution in pentane and 1.6 M ^{n}BuLi in hexanes were purchased from Acros Organics, and $^iPr_2SiCl_2$ was purchased from Geleste. These reagents were used as received.

^{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. Mass spectrometry was carried out on a Hewlett-Packard 5890A equipped with a 5970 mass selective detector and a DB-1, 0.25 μm film, fused silica capillary column with an injection temperature of 250 °C, an initial column temperature of 40 °C, a ramp rate of 10 °C/min, and a final temperature of 280 °C.

Single crystals 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 molybednum X-ray tube ($\lambda = 0.71073$ Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Elemental analyses were carried out by Robertson Microlit Labs, Inc.,

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[30] (a) Reddy, K. P.; Petersen, J. L. *Organometallics* **1989**, *8*, 547. (b) Bochman, M.; Lancaster, S. J.; Hursthouse, M. D.; Mazid, M. *Organometallics* **1993**, *12* 4718. (c) van der Hende, J. R.; Hessen, B.; Meetsma, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 537.

[31] For example addition of hydrogen to Cp''_2ZrMe_2, $Cp^*Cp''ZrMe_2$, and *rac*-$(1\text{-}CMe_3C_9H_6)_2ZrMe_2$ produced no reaction. The *ansa*-zirconocene $^iPr_2Si(\eta^5\text{-}3\text{-}SiMe_3C_5H_3)(\eta^5\text{-}3,4\text{-}(SiMe_3)_2C_5H_2)ZrMe_2$ undergoes hydrogenolysis over the course of 1 week, affording trace amounts of **10**. Pool, J. A.; Bradley, C. A.; Chirik, P. J. Unpublished results.

[32] Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; ACS Symposium Series No. 357; Wayda, A. L., Darensbourg, M. Y. Eds.; American Chemical Society: Washington, D.C., 1987; Chapter 4.

[33] Pangborn, A.; Giardello, M.; Grubbs, R. H.; Rosen, R.; Timmers. F. *Organometallics* **1996**, *15*, 1518.

[34] Antiñolo, A.; Lappert, M. F.; Singh, A.; Winterborn, J. W.; Engelhardt, L. M.; Raston, C. L.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc. Dalton Trans.* **1987**, 1463.

Madison, NJ. The zirconocene isobutyl hydride complexes could only be isolated as thick oils, precluding elemental analyses, while others were consistently low due to incomplete combustion. Representative ^{1}H NMR spectra are included in the Supporting Information to establish purity.

Preparation of Cp*Cp″ZrCl$_2$ (1). A 100 mL round-bottom flask was charged with 0.632 g (3.00 mmol) of $C_5H_4(SiMe_3)_2$ and 50 mL of THF. The clear solution was chilled in the cold well, and 1.9 mL (3.0 mmol) of 1.6 M ^{n}BuLi was added dropwise via pipet. The resulting reaction mixture was warmed to room temperature and stirred for 3 h, after which time 1.00 g (3.01 mmol) of Cp*ZrCl$_3$ was added in small portions. The reaction mixture was stirred for 6 h, and the THF was removed in vacuo. The resulting oily solid was dissolved in diethyl ether, and the white precipitate was removed via filtration through Celite. The Celite was washed several times with fresh diethyl ether. The solvent was removed in vacuo, leaving a white powder, which upon recrystallization from pentane afforded 1.01 g (67%) of **1**. Anal. Calcd for $C_{21}H_{36}Si_2ZrCl_2$: C, 49.75; H, 7.16. Found: C, 49.53; H, 6.80. ^{1}H NMR (benzene-d_6): δ 0.31 (s, 18H, SiMe_3), 1.83 (s, 15H, C_5Me_5), 5.98 (m, 2H, Cp), 6.91 (m, 1H, Cp). ^{13}C NMR (benzene-d_6): δ 0.26 (SiMe_3), 12.63 (C_5Me_5), 119.56, 127.00, 138.80 (Cp″), 124.35 (C_5Me$_5$).

Preparation of Cp*Cp″Zr(H)Cl (2). A 20 mL scintillation vial containing 0.115 g (0.227 mmol) of **1** in approximately 10 mL of toluene was frozen in the cold well. To the thawing solution, 152 μL (0.228 mmol) of 1.5 M ^{t}BuLi in pentane was added via microsyringe. The reaction mixture was stirred and warmed to room temperature, after which time it was immediately filtered through a pad of Celite. Removal of the toluene in vacuo and washing with pentane affords 0.96 g (85%) of **2** as a yellow foam. Analytically pure material may be obtained by chilling concentrated pentane solutions. Anal. Calcd for $C_{21}H_{37}Si_2ZrCl$: C, 53.37; H, 7.90. Found: C, 53.14 H, 7.58. ^{1}H NMR (benzene-d_6): δ 0.30, 0.37 (s, 18H, SiMe_3), 1.90 (s, 15H, C_5Me_5), 4.93, 5.70, 6.50 (m, 3H, Cp), 6.33 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 0.61, 0.69 (SiMe_3), 12.76 (C_5Me_5), 117.19 (C_5Me$_5$), 118.10, 120.08, 124.74, 126.10, 129.43 (Cp).

Preparation of Cp″$_2$Zr(H)Cl (3). In the drybox, a swivel frit assembly was charged with 0.37 g (0.825 mmol) of Cp″$_2$-ZrCl$_2$. On the vacuum line, approximately 50 mL of toluene was added by vacuum transfer. At −78 °C, 550 μL (0.825 mmol) of 1.5 M ^{t}BuLi in pentane was added via microsyringe. Upon addition, a dark green solution was formed. The precipitate was removed via filtration and was washed with recycled pentane, affording 0.96 g (90%) of **3** as a waxy yellow solid. Recrystallization from pentane at −35 °C affords analytically pure yellow blocks. Anal. Calcd for $C_{22}H_{43}Si_4Zr_1Cl_1$: C, 48.32; H, 7.93. Found: C, 47.56, H, 7.45. ^{1}H NMR (benzene-d_6): δ 0.31, 0.33 (s, 18H, SiMe_3), 5.57, 6.07, 6.84 (m, 3H, Cp), 6.22 (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 0.36 (SiMe_3), 114.15, 115.75, 125.30, 127.48, 127.18 (Cp).

Preparation of Cp*Cp″Zr(CH$_2$CHMe$_2$)H (4). In the drybox, a 20 mL scintillation vial was charged with 0.100 g (0.198 mmol) of **1** and approximately 10 mL of toluene. The yellow solution was frozen in the cold well. To the thawing, stirred solution, 329 μL (0.396 mmol) of a 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, leaving 0.078 g (80%) of **4** as a thick brown oil. ^{1}H NMR (benzene-d_6): δ −0.32, −0.29 (d, 2H, CH_2CH(CH$_3$)$_2$), 0.23 (s, 9H, SiMe_3), 0.39 (s, 9H, SiMe_3), 0.92, 0.93 (s, 6H, CH$_2$CH(CH_3)$_2$), 1.89 (s, 15H, C_5Me_5), 5.06, 5.37, 5.80 (m, 3H, Cp″), 6.83 (m, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 0.870, 0.901 (SiMe_3), 12.61 (C_5Me_5), 70.95 (CH$_2$CHMe$_2$), 32.44 (CH$_2$$CHMe_2$), 29.59 (CH$_2CHMe_2$), 29.65 (CH$_2CHMe_2$), 117.84 ($C_5Me_5$), 115.77, 116.18, 117.85, 118.11 (Cp″).

Preparation of Cp*Cp″ZrH$_2$ (5). In the drybox, a J. Young NMR tube was charged with 20 mg of **4**, and the sample was dissolved in toluene-d_8. 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 (toluene-d_8): δ 0.26 (s, 18H, SiMe_3), 2.00 (s, 15H, C_5Me_5), 5.21 (m, 2H, Cp″), 6.89 (m, 2H, Zr-*H*), 7.06 (m, 1H, Cp″). ^{13}C NMR (benzene-d_6): δ 0.871 (SiMe_3), 13.46 (C_5Me_5), 119.63 (C_5Me$_5$), 112.93, 116.62, 124.10 (Cp).

Preparation of Cp*(η^5-1-SiMe$_3$,η^1-3-SiMe$_2$CH$_2$C$_5$H$_3$)ZrH (6). A J. Young NMR tube was charged with 20 mg of freshly prepared **5** and dissolved in benzene-d_6. The solution was frozen, the tube evacuated, and the reaction then monitored by ^{1}H NMR spectroscopy. Quantitative conversion to **6** was achieved over the course of 16 h. Anal. Calcd for $C_{21}H_{33}Si_2Zr_1$: C, 58.24; H, 7.69. Found: C, 57.60; H, 7.17. ^{1}H NMR (benzene-d_6) δ 0.35 (s, 9H, SiMe_3), 0.19, 0.50 (s, 6H, Me_2Si), 1.22, (s, 2H, Zr-CH_2), 1.89 (s, 15H, C_5Me_5), 5.18, 5.49, 5.89 (m, 1H, (Me$_3$-Si)CpH_3(Me$_2$Si)), 6.86 (m, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ −1.94 (Me_2Si), 1.44 (SiMe_3), 4.24 (Me_2Si), 13.29 (C_5Me_5), 50.82 (CH$_2$), 112.15, 115.12, 116.26, 117.75, 123.76 ((Me$_3$Si)CpH$_3$(Me$_2$-Si)), 118.82 (C_5Me$_5$).

Preparation of ^{i}Pr$_2$Si(η^5-3-SiMe$_3$C$_5$H$_4$)(η^5-3,4-(SiMe$_3$)$_2$-C$_5$H$_3$) (7). In the drybox, a 250 mL round-bottom flask was charged with 3.581 g (10.00 mmol) of ^{i}Pr$_2$Si(C$_5$H$_3$(SiMe$_3$)$_2$)Cl and approximately 150 mL of THF. To this solution, 1.763 g (10.00 mmol**)** of K[SiMe$_3$Cp] was added. A reflux condenser and 180° needle valve were attached. The reaction mixture was refluxed for 3 days, after which the solvent was removed in vacuo. In the drybox, pentane was added to the resulting orange oil, and the white precipitate was removed via filtration through a pad of Celite. The solvent was removed in vacuo, leaving 4.27 g (93%) of an orange oil. ^{1}H NMR (benzene-d_6): δ −0.033, −0.023, 0.035 (s, 27H, SiMe_3), 1.20 (d, 12H, CHMe_2), 1.1−1.3 (m, 2H, CHMe$_2$), 6.51, 6.55, 6.79, 6.90, 6.92, 6.72, 7.00, 7.01 (d, 5H, *Cp*). MS: $M^+ = 460$ M/Z, $RT = 23.78$ min.

Preparation of ^{i}Pr$_2$Si(η^5-3-SiMe$_3$C$_5$H$_3$)(η^5-3,4-(SiMe$_3$)$_2$-C$_5$H$_2$)ZrCl$_2$ (8). In the drybox, a 250 mL round-bottom flask was charged with 4.271 g (9.27 mmol) of ^{i}Pr$_2$Si(Cp(SiMe$_3$)$_2$)-(CpSiMe$_3$) and approximately 150 mL of toluene along with 5 mL of THF. To this solution, 2.380 g (10.21 mmol) of ZrCl$_4$ was added. A reflux condenser and 180° needle valve were attached. The reaction mixture was refluxed for 3 days, after which the solvent was removed in vacuo. In the drybox, diethyl ether was added to the resulting orange oil and the white precipitate was removed via filtration through a pad of Celite. The Celite was washed several times with diethyl ether. The solvent was removed in vacuo, leaving an orange oil, which upon recrystallization from pentane afforded 2.40 g (40%) of **8** as a yellow powder. Anal. Calcd for $C_{25}H_{46}Si_4ZrCl_2$: C, 49.12; H, 5.94. Found: C, 48.93 H, 5.78. ^{1}H NMR (benzene-d_6): δ 0.44, 0.46, 0.54 (s, 27H, SiMe_3), 1.15, 1.16 (dd, 12H, CHMe_2), 1.2−1.3 (m, 2H, CHMe$_2$), 5.99, 6.36, 6.99 (t, 3H, Me$_3$SiCp), 6.41, 6.66 (d, 2H, (Me$_3$Si)$_2$$Cp$. ^{13}C NMR (benzene-$d_6$): δ 0.20, 0.89, 1.39 (SiMe_3), 18.10, 18.13, 18.27 (CHMe_2), 10.86, 12.28 (CHMe$_2$) 108.21, 111.26, 116.08, 124.11, 128.41, 132.54, 134.01, 138.16, 138.38, 148.80 (Cp).

Preparation of ^{i}Pr$_2$Si(η^5-3-SiMe$_3$C$_5$H$_3$)(η^5-3,4-(SiMe$_3$)$_2$-C$_5$H$_2$)Zr(CH$_2$CHMe$_2$)(H) (9). A 20 mL scintillation vial was charged with 0.405 g (0.675 mmol) of **8** and approximately 5 mL of toluene, and the yellow solution was frozen in the cold well. To the thawing solution, 871 μL (1.30 mmol) of 1.5 M ^{t}BuLi in pentane was added dropwise via microsyringe. The reaction mixture was warmed to room temperature and stirred for 5 min and filtered through Celite. The toluene was removed in vacuo, leaving 0.42 g (87%) of a thick brown oil. ^{1}H NMR (benzene-d_6): δ 0.39, 0.42, 0.49 (s, 27H, SiMe_3), 0.86, 0.87 (s, 6H, CH$_2$CHMe_2), 1.14, 1.25 (m, 12H, CHMe_2), 1.2−1.5 (m, 2H, CHMe$_2$), 2.46 (m, 1H, CH$_2$CHMe$_2$), 4.89, 5.66, 6.15, 6.57, 6.64 (m, 5H, Cp), 5.38, (s, 1H, Zr-*H*). ^{13}C NMR (benzene-d_6): δ 0.632, 1.67, 2.15 (SiMe_3), 11.53, 11.79 (Si(CHMe$_2$)$_2$), 18.23, 18.28, 18.47, 18.60 (Si(CHMe_2)$_2$), 35.83 (ZrCH$_2$CHMe$_2$), 27.19, 29.55 (ZrCH$_2$CHMe_2), 98.04, 100.03, 100.57, 115.28, 117.21, 121.34, 121.51, 124.76, 132.93, 133.16 (Cp).

Preparation of [^{i}Pr$_2$Si(η^5-3-SiMe$_3$C$_5$H$_3$)(η^5-3,4-(SiMe$_3$)$_2$-C$_5$H$_2$)ZrH$_2$]$_2$ (10). A J. Young NMR tube was charged with 10 mg of **9** and approximately 0.5 mL of benzene-d_6. On the high-vacuum line, the tube was degassed using standard freeze−pump−thaw techniques, and 1 atm of dihydride was admitted at −196 °C. The tube was thawed and shaken and the reaction monitored by ^{1}H NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ −4.37 (m, 2H, Zr-H_b), 0.47, 0.49, 0.60 (s, 27H, SiMe_3), 0.85, 0.87 (d, 12H, CHMe_2), 1.1−1.4 (m, 2H, CHMe$_2$), 4.02 (t, 2H, Zr-H_t), 5.06, 6.22, 6.51 (s, 3H, Me$_3$SiCp), 5.42, 6.72 (d, 2H, (Me$_3$Si)$_2$$Cp$). ^{13}C NMR (benzene-$d_6$): δ 1.73, 2.82, 2.93 (SiMe_3), 11.45, 12.50 (Si(CHMe$_2$)$_2$), 18.48, 18.53, 18.71, 19.08 (Si(CHMe_2)$_2$), 96.45, 106.40, 113.55, 113.74, 115.12, 115.95, 122.48, 123.94, 125.12, 136.30 (Cp).

Preparation of *rac*-(1-CMe$_3$-C$_9$H$_6$)$_2$Zr(H)Cl (12). A 20 mL scintillation vial was charged with 0.225 g (0.446 mmol) of **11**, and 5 mL of toluene was added. The yellow slurry was chilled in the cold well. To the stirred solution, 0.054 g (0.443 mmol) of solid NaBEt$_3$H was added. The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting black solution was filtered through Celite, and the toluene was removed in vacuo. Recrystallization from pentane affords 0.058 g (27%) of a yellow-green solid. Anal. Calcd for C$_{26}$H$_{31}$Cl$_1$Zr$_1$C, 66.42; H, 6.65. Found: C, 66.03; H, 6.27. ^{1}H NMR (benzene-d_6): δ 1.41 (s, 18H, CMe_3), 4.56 (s, 1H, ZrH), 6.25 (s, 2H, Cp), 6.71 (t, 5.3 Hz, 2H, Ind), 6.76 (s, 2H, Cp), 6.85 (t, 5.2 Hz, 2H, Ind), 7.01 (d, 8.8 Hz, 2H, Ind), 7.61 (d, 8.7 Hz, 2H, Ind). ^{13}C NMR (benzene-d_6): δ 32.14 (CMe_3), 93.66 (Cp), 96.48 (Cp), 115.26 (Ind), 122.19 (Ind), 124.32 (Ind), 124.63 (Ind), 125.44 (Ind), 125.80 (Ind), 126.30 (Ind), *not located* (CMe$_3$).

Preparation of *rac*-(1-CMe$_3$-C$_9$H$_6$)$_2$Zr(CH$_2$CHMe$_2$)(H) (13). A 20 mL scintillation vial was charged with 0.106 g (0.210 mmol) of **11**, and approximately 5 mL of toluene was added. The yellow slurry was frozen in the cold well. To the thawing reaction mixture, 137 μL (0.205 mmol) of 1.5 M ^{t}BuLi in pentane was added via microsyringe. The yellow reaction mixture was warmed to room temperature and stirred for 1 h and then filtered through a pad of Celite. The toluene was removed in vacuo, leaving 0.086 g (84%) of a honey brown oil. ^{1}H NMR (benzene-d_6): δ −0.68 (m, 1H, CH_2CHMe$_2$), 0.71 (m, 1H, CH_2CHMe$_2$), 0.724 (d, 6.8 Hz, 3H, CH$_2$CHMe_2), 0.768 (d, 5.2 Hz, 3H, CH$_2$CHMe_2), 1.40 (s, 9H, CMe_3), 1.53 (s, 9H, CMe_3), 2.07 (m, 1H, CH$_2$CHMe$_2$), 3.33 (s, 1H, ZrH), 4.73, 5.87, 6.01, 6.51 (Cp), 6.63, 6.75, 6.97, 7.26, 7.44, 7.59 (Ind). ^{13}C NMR (benzene-d_6): δ 32.72, 32.86 (CMe_3), 136.26, 143.25 (CMe$_3$), 83.94 (CH$_2$CHMe$_2$), 21.42 (CH$_2$$CHMe_2$), 30.70, 32.23 (CH$_2$-CH$Me_2$), 90.43, 91.35, 92.18, 92.30, 93.75, 96.64 (Cp), 113.10, 115.34, 117.32, 120.26, 121.49, 122.98, 123.80, 124.73, 125.27, 1 *not located* (Ind).

Acknowledgment. We would like to thank the Department of Chemistry and Chemical Biology at Cornell University for generous financial support. We are grateful to Emil Lobkovsky for experimental assistance with X-ray diffraction and to Bosong Xiang for guidance in obtaining NOESY spectra. C.A.B. would like to thank the National Science Foundation for a predoctoral fellowship.

Supporting Information Available: Crystallographic data for **2**, **8**, and **12** including complete atom labeling schemes, tables of atomic coordinates, and complete bond distances and angles. Representative ^{1}H NMR spectra of zirconocene isobutyl hydride complexes and NOESY data for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM011090Z