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Synthesis of Bis(indenyl)zirconium Dihydrides and Subsequent Rearrangement to η^5,η^3-4,5-Dihydroindenediyl Ligands: Evidence for Intermediates during the Hydrogenation to Tetrahydroindenyl Derivatives

Christopher A. Bradley, Emil Lobkovsky, Ivan Keresztes, and Paul J. Chirik*

Contribution from the Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received January 27, 2006; E-mail: pc92@cornell.edu

Abstract: Exposure of η^9,η^5-bis(indenyl)zirconium sandwich complexes to 4 atm of H_2 resulted in facile oxidative addition to furnish the corresponding zirconocene dihydrides, $(\eta^5\text{-}C_9H_5\text{-}1,3\text{-}R_2)_2ZrH_2$ (R = $SiMe_3$, $SiMe_2Ph$, $CHMe_2$). Continued hydrogenation completed conversion to the tetrahydroindenyl derivatives, $(\eta^5\text{-}C_9H_9\text{-}1,3\text{-}R_2)_2ZrH_2$. Deuterium labeling studies established that dihydrogen (dideuterium) addition to the benzo rings is intramolecular and stereospecific, occurring solely from the endo face of the ligand, proximal to the zirconium. In the absence of dihydrogen, the bis(indenyl)zirconium dihydrides rearranged to new zirconium monohydride complexes containing an unusual η^5,η^3-4,5-dihydroindenediyl ligand, arising from metal-to-benzo ring hydrogen transfer. Mechanistic studies, including a normal, primary kinetic isotope effect measured at 23 °C, are consistent with a pathway involving regio- and stereoselective insertion of a benzo C=C bond into a zirconium hydride. The stereochemistry of the insertion reaction, and hence the η^5,η^3-4,5-dihydroindenediyl product, is influenced by the presence of donor ligands and controlled by the preferred conformation of the indenyl rings. Exposure of the zirconium hydrides containing the η^5,η^3-4,5-dihydroindenediyl rings to 1 atm of dihydrogen afforded the tetrahydroindenyl zirconium dihydride complexes, establishing the intermediacy of this unusual coordination environment during benzo ring hydrogenation.

Introduction

Oxidative addition, whereby a transition metal increases in formal oxidation state by two units, is a fundamental transformation in organometallic chemistry and constitutes a key step in numerous catalytic cycles.[1] While oxidative addition has been well studied and amply precedented in late transition metal chemistry,[2] observation of oxidative addition processes with early transition metal complexes remains rare. This discrepancy is due, in part, to the paucity of isolable early metal complexes with low oxidation states.[3] Despite the limited number of examples, oxidative addition reactions with reduced early metal compounds could serve as a powerful synthetic tool to access unique structures that are unavailable from alternative preparative routes.

In organozirconium chemistry, seminal studies from Schwartz and co-workers described the formal oxidative addition of alkyl halides to $(\eta^5\text{-}C_5H_5)_2ZrL_2$ (L = PPh_2Me, PMe_2Ph) species.[4] Detailed mechanistic and spectroscopic studies[5] are consistent with a series of one-electron steps involving both metal-centered and organic radicals. This behavior contrasts the two-electron processes typically encountered with late metal complexes.[2] Oxidative addition of alkenyl halides to Negishi's reagent, $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ treated with 2 equiv of ^{n}BuLi, has proven useful in numerous coupling and transmetalation reactions,[6] and isolation and structural characterization of an alkenylzirconocene chloride product have been achieved.[7] In some cases, oxidative addition is also believed to play a key role in the activation of fluorocarbons by reduced zirconium complexes.[8]

Well-defined addition of nonpolar reagents such as silanes and dihydrogen to reduced group 4 metallocene complexes is also rare. Exposure of the end-on bound dinitrogen complex, $[(\eta^5\text{-}C_5Me_5)_2Zr(\eta^1\text{-}N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, to 1 atm of dihydrogen results in rapid oxidative addition of H_2 to yield the monomeric dihydride complex, $(\eta^5\text{-}C_5Me_5)_2ZrH_2$.[9] Similar observations have

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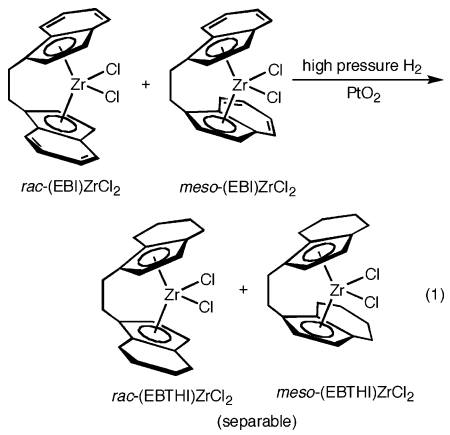
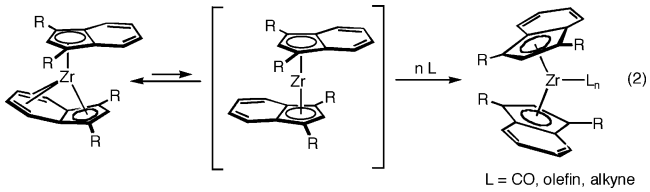
been reported with the related "mixed ring" compound, $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4H)Zr(\eta^1\text{-}N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, to furnish $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4H)ZrH_2$.[10] Zirconocene and hafnocene silyl hydride complexes, $(\eta^5\text{-}C_5H_5)_2M(SiPh_3)(H)$, have also been prepared by apparent oxidative addition to phosphine-stabilized Negishi-type precursors. However, mechanistic studies are consistent with an addition−elimination pathway rather than oxidative addition.[11] In contrast, oxidative addition of secondary silanes has been implicated in the catalytic hydrosilation of olefins promoted by $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}CH_2{=}CHEt)$.[12]

The interaction of dihydrogen with bis(indenyl)zirconium compounds is of both fundamental and practical importance, given the utility of these compounds in olefin polymerization[13] and other catalytic bond-forming reactions.[14−16] The high-pressure, PtO_2-catalyzed hydrogenation of *ansa*-bis(indenyl)-zirconocene dichloride complexes to the corresponding tetrahydroindenyl derivatives serves as an important synthetic method for the separation of racemo and meso isomers (eq 1).[17,18] Hydrogenation of propagating zirconocene alkyl species in α-olefin polymerization has also been identified as an important and sometimes deleterious chain-transfer pathway, reducing polymer molecular weights and limiting the industrial utility of many catalysts.[19]



Bis(indenyl)zirconium dihydride complexes are attractive targets, given their potential in both stoichiometric and catalytic transformations. In addition, complexes of this type could serve as important mechanistic models for the initiating and propagating species in olefin polymerization,[20] providing insight into key fundamental steps related to chain propagation, termination, and stereoselectivity.[21] Attempts to prepare such species have been unsuccessful, as H_2 addition to the requisite zirconium alkyl precursor is often accompanied by benzo ring hydrogenation. For example, hydrogenation of bis(indenyl)zirconium dimethyl requires high temperature and pressure (80 atm, 140 °C) and furnishes the bis(tetrahydroindenyl)zirconium dihydride dimer.[22] Similar reactivity has been observed in mixed indenyl cyclopentadienyl chemistry, as $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)ZrMe_2$ undergoes hydrogenation at ambient temperature and pressure to yield $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_9H_{11})ZrH_2]_2$.[23]

Recently, our laboratory has reported the synthesis[24] and characterization[25] of the first examples of η^9,η^5-bis(indenyl)-zirconium sandwich complexes. In the ground state, η^9 coordination of one of the indenyl rings is observed, where all nine carbons of the carbocycle are bonded to the zirconium. Both solution spectroscopic[25] and computational studies[26] have demonstrated that dissociation of the coordinated benzo ring is facile in solution and the η^5,η^5-bis(indenyl)zirconocene is accessible at ambient temperature (eq 2). While detailed kinetic and mechanistic studies have yet to be performed, preliminary reactivity studies support this view, as facile coordination of CO,[24] coupling of olefins and alkynes,[25] and C−H activation of *N*,*N*-dimethylaminopyridine (DMAP)[24] have been observed at ambient temperature. In each example, the familiar η^5,η^5-hapticity of the indenyl rings has been restored.[27]



Perhaps more striking is the reactivity of the η^9,η^5-bis-(indenyl)zirconium sandwich complexes with principally σ-donating ligands. Addition of cyclic or chelating ethers such as tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) produced an unexpected haptotropic rearrangement, whereby the zirconium migrates to the benzo ring of one indenyl ligand (eq 3).[28] Kinetic studies established a first-order dependence on the incoming ligand, suggesting a mechanism involving direct attack of the incoming nucleophile on the complex bearing the strained η^9-indenyl ring. Taken together, the structure and resulting reactivity of η^9,η^5-bis(indenyl)zirconium sandwich compounds

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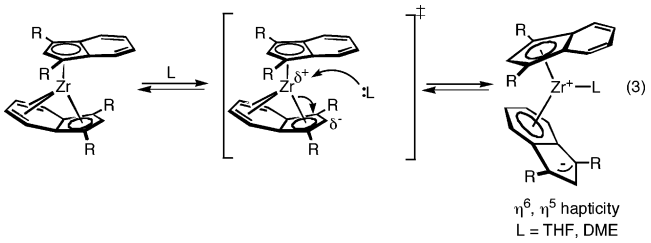
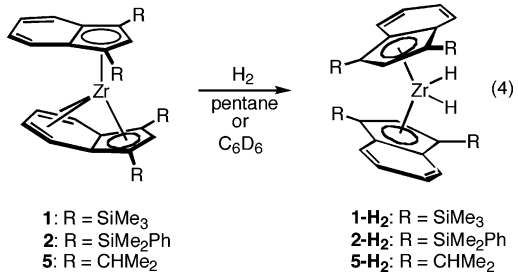
highlight the ability of the 10-π-electron indenyl ligand to smoothly adjust hapticity to meet the electronic requirements of the metal.



Oxidative addition of dihydrogen to the η^9,η^5-bis(indenyl)-zirconium sandwich complexes seemed a viable synthetic method for the preparation of elusive bis(indenyl)zirconocene dihydrides. This reaction class was also of interest to determine the hapticity of the indenyl rings in the final product as well as the preferred mechanistic pathway to reach this configuration. Here we describe the synthesis and crystallographic characterization of the first examples of η^5,η^5-bis(indenyl)zirconium dihydride complexes prepared by formal oxidative addition of H_2 to the corresponding η^9,η^5-sandwich compounds. In the absence of H_2, the resulting dihydrides undergo facile regio- and stereoselective hydride-to-benzo ring migration to furnish unusual η^5,η^3-4,5-dihydroindenediyl ligands. A combination of structural, spectroscopic, isotopic labeling, and kinetic studies have been used to elucidate the mechanism of the rearrangement and identify these complexes as intermediates in the hydrogenation to the corresponding tetrahydroindenyl derivatives.

Results and Discussion

Synthesis of η^5,η^5-Bis(indenyl)- and η^5,η^5-Bis(tetrahydroindenyl)zirconium Dihydrides. Our investigations into oxidative addition reactions with η^9,η^5-bis(indenyl)zirconium sandwich compounds commenced with the addition of 4 atm of H_2 to (η^9-C_9H_5-1,3-R_2)(η^5-C_9H_5-1,3-R_2)Zr (R = $SiMe_3$, **1**; $SiMe_2Ph$, **2**; $CHMe_2$, **5**).[29] In each case, a color change from burgundy to bright yellow was observed immediately upon exposure of the compound to dihydrogen at 23 °C. Analysis of the resulting benzene-d_6 solutions by ^1H and ^{13}C NMR spectroscopy indicated complete and quantitative conversion to new C_{2v}-symmetric products, assigned as the η^5,η^5-bis(indenyl)-zirconium dihydrides (η^5-C_9H_5-1,3-R_2)$_2$ZrH_2 (R = $SiMe_3$, **1-H$_2$**; $SiMe_2Ph$, **2-H$_2$**; $CHMe_2$, **5-H$_2$**) (eq 4).



Notably, ^1H and ^{13}C NMR spectra recorded in benzene-d_6 exhibit the appropriate number of aromatic resonances, demonstrating that the benzo rings have remained intact and did not undergo hydrogenation. At typical NMR concentrations of 0.02−0.04 M, downfield-shifted Zr−*H* resonances were observed in the ^1H NMR spectra (Table 1), consistent with monomers in solution.[23] Confirmation of these peak assignments has been accomplished by deuterium labeling and by exposure of the dihydride complexes to additional H_2. The presence of even trace amounts of H_2 resulted in broadening and ultimately disappearance of the metal hydride resonance, establishing exchange between the Zr−*H* bonds and the free gas on the NMR time scale. This behavior is typical of monomeric zirconocene dihydrides.[23]

Table 1. ^1H NMR Chemical Shifts of Bis(indenyl)- and Bis(tetrahydroindenyl)zirconium Dihydrides

compound	δ Zr–*H* (ppm)[a]	compound	δ Zr–*H* (ppm)[a]
1-H$_2$	6.49	**1-THI-H$_2$**	6.61
2-H$_2$	6.95	**2-THI-H$_2$**	6.78
5-H$_2$	6.86	**5-THI-H$_2$**	7.07

[a] Spectra recorded in benzene-d_6 at 23 °C.

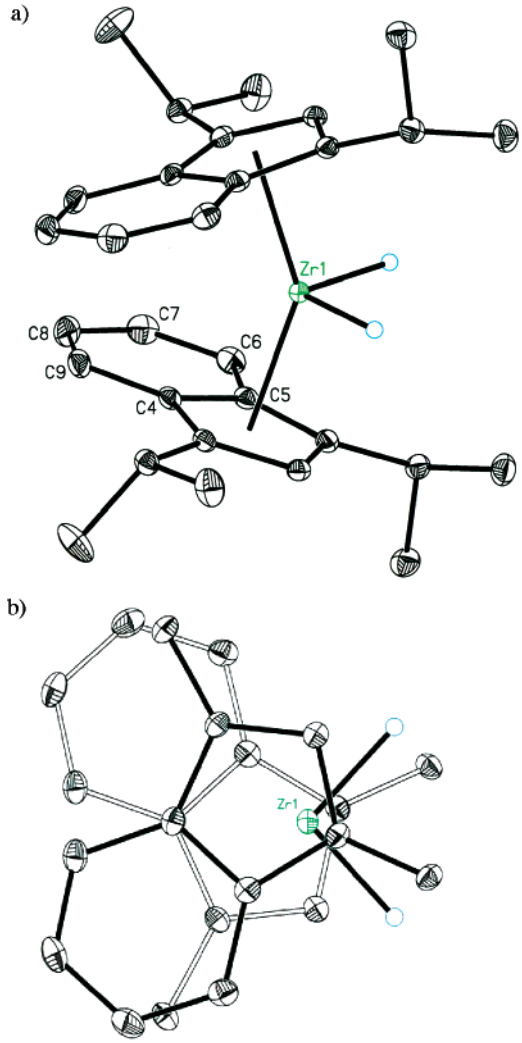
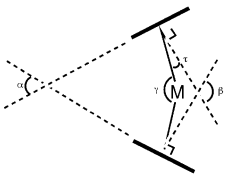


Figure 1. (a) Molecular structure of **5-H$_2$** at 30% probability ellipsoids. Hydrogen atoms, except for the zirconium hydrides, are omitted for clarity. (b) Top view of the molecule at 30% probability ellipsoids. Isopropyl methyl substituents and hydrogen atoms, except for the zirconium hydrides, are omitted for clarity.

The solid-state structure of **5-H$_2$** was determined by X-ray diffraction, a representation of which is shown in Figure 1. Selected metrical parameters are reported in Table 2. The data were of sufficient quality that all of the hydrogen atoms, including the zirconium hydrides, were located and freely refined. In the solid state, the indenyl ligands adopt an essentially

Table 2. Selected Bond Distances and Angles for **5-H_2** and **5-H_2(PMe_3)**



α = interplanar-ring angle

$\beta = Cp_{norm}\text{-}Cp_{norm}$; $\alpha + \beta = 180°$

$\gamma = Cp_{cent}\text{-}M\text{-}Cp_{cent}$

τ = tilt angle, $0.5(\gamma - \beta)$

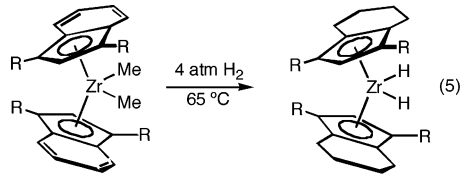
parameter	**5-H_2**	**5-H_2(PMe_3)**
Zr(1)−H(1M)	1.74(2) Å	1.741(19) Å; 1.785(19) Å
C(6)−C(7)	1.362(2) Å	
C(8)−C(9)	1.371(2) Å	
H(1M)−Zr(1)−H(1M′)	95.6(2)°	129.0(9)°
α	33.2(3)°	47.6(2)°
β	146.8(3)°	132.4(2)°
γ	144.8(3)°	136.3(2)°
τ	−1	2
rotational angle[a]	88.7(3)°	163.2(3)°

[a] Dihedral angle formed between the planes defined by the metal and C(2) indenyl carbon and the midpoint of the bond in the ring fusion.

gauche conformation, with a rotational angle of 88.7(3)° and an idealized C_2 axis bisecting the two zirconium hydride positions. The isopropyl substituents are oriented with the methine hydrogens directed toward the zirconium, minimizing transannular steric interactions. One isopropyl group on each ring lies over the zirconocene wedge and most likely serves to prevent formation of hydride bridges and subsequent dimerization. The carbon−carbon bond distances in the planar six-membered rings range between 1.362(2) and 1.418(2) Å, confirming their identity as sp^2-hybridized carbons with intact benzo rings.

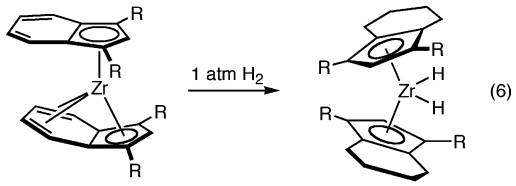
Formal oxidative addition of H_2 to the η^9,η^5-bis(indenyl)-zirconium sandwich compounds provides the first access to zirconium dihydride complexes where the indenyl rings remain intact.[30] To our knowledge, the only other examples of early metal hydride complexes with indenyl ligands are a family of *ansa*-lanthanidocene hydrides, prepared by treatment of the monoamide complexes with diisobutylaluminum hydride.[31] However, isomerization of the ansa ligand to a "flyover" structure, whereby the two [$SiMe_2$]-linked indenyl rings bridge two metal centers, accompanies preparation of the metal hydrides.

To illustrate the importance of the oxidative addition route to bis(indenyl)zirconocene dihydrides, the traditional method for the synthesis of zirconocene hydrides, namely hydrogenation of a dialkyl precursor, was also explored. Exposure of the bis-(indenyl)zirconocene dimethyl complex, (η^5-C_9H_5-1,3-($SiMe_3$)$_2$)$_2$-$ZrMe_2$ (**1-Me_2**), to 4 atm of H_2 resulted in hydrogenation to the bis(tetrahydroindenyl) derivative, **1-THI-H_2** (eq 5). Monitoring the hydrogenation reaction by ^{1}H NMR spectroscopy provided no evidence for the bis(indenyl)zirconocene dihydride, **1-H_2**, suggesting that initial hydrogenolysis of the zirconium alkyl proceeds with a higher kinetic barrier than subsequent ring hydrogenation. Performing a similar procedure with **5-Me_2** produced no reaction, even after heating to 85 °C for 2 days.



1-Me_2: R = $SiMe_3$ **1-THI-H_2**: R = $SiMe_3$

The bis(tetrahydroindenyl)zirconium dihydrides, **1-THI-H_2** and **5-THI-H_2**, were readily prepared by continued hydrogenation of the corresponding bis(indenyl)zirconium dihydrides at 23 °C (eq 6). Preparative scale reactions of **5-THI-H_2** were typically carried out at 65 °C for convenience. Special care must be taken during the preparation of **1-H_2** and **2-H_2**, as exposure of the η^9,η^5-bis(indenyl)zirconium sandwich to dihydrogen for more than a few minutes leads to significant benzo ring hydrogenation. In contrast, the hydrogenation of **5-H_2** to **5-THI-H_2** was much slower, requiring days to reach completion at 23 °C and 1 atm of H_2, making isolation of the bis(indenyl)-zirconium dihydride relatively straightforward. The observation of ring hydrogenation from **5-H_2** but not **5-Me_2** further underscores the higher barrier associated with Zr−Me hydrogenolysis as compared to ring reduction.



1: R = $SiMe_3$
5: R = $CHMe_2$

1-THI-H_2: R = $SiMe_3$
5-THI-H_2: R = $CHMe_2$

To determine if an impurity in **1-H_2** was catalyzing benzo ring hydrogenation and producing artificially faster rates, the hydrogenation of a nearly equimolar mixture of **1-H_2** and **5-H_2** was monitored by ^{1}H NMR spectroscopy. Gratifyingly, each compound in the mixture hydrogenated to the tetrahydroindenyl derivative at a rate similar to that of the independent trials, suggesting that the observed differences in hydrogenation rates are intrinsic to the compounds rather than a result of impurities.

Regardless of the synthetic method used, the bis(tetrahydroindenyl)zirconium dihydrides were isolated in high yield as off-white powders. Hydrogenation of the benzo rings was readily identified by ^{1}H NMR spectroscopy. Resonances in the vicinity of 1.7−2.8 ppm were observed for the saturated six-membered rings. Downfield-shifted Zr−*H* peaks (Table 1) were noted in each case, indicative of monomers in benzene-d_6 solution. As with the analogous bis(indenyl) complexes, exchange with free H_2 was observed on the NMR time scale.

The silyl-substituted bis(tetrahydroindenyl)zirconium dihydride, **1-THI-H_2**, was also characterized by X-ray diffraction. A representation of the molecular structure is shown in Figure 2, and selected metrical parameters are reported in Table 3. In the solid state, nearly ideal C_2 symmetry is observed, with the

(28) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291.
(29) The numbering scheme used throughout this paper is adopted from the following: Bradley, C. A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H. D.; Chirik, P. J. *Organometallics* **2004**, *23*, 5332. The nomenclature for **8-H_2** and subsequent rearranged products is taken from ref 25.
(30) Examples of metal hydrides with indenyl ligands: Fe: (a) Ahmed, H.; Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K. *Inorg. Chim. Acta* **1989**, *164*, 5. (b) Ahmed, H.; Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K. *J. Organomet. Chem.* **1991**, *418*, C14. Tl: (c) Kumar, N.; Sharma, R. K. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2625. Ce (d) Kapur, S.; Kalsotra, B. L.; Multani, R. K. *J. Inorg. Nucl. Chem.* **1974**, *36*, 932.
(31) Klimpel, M. G.; Sirsch, P.; Scherer, W.; Anwander, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 574.

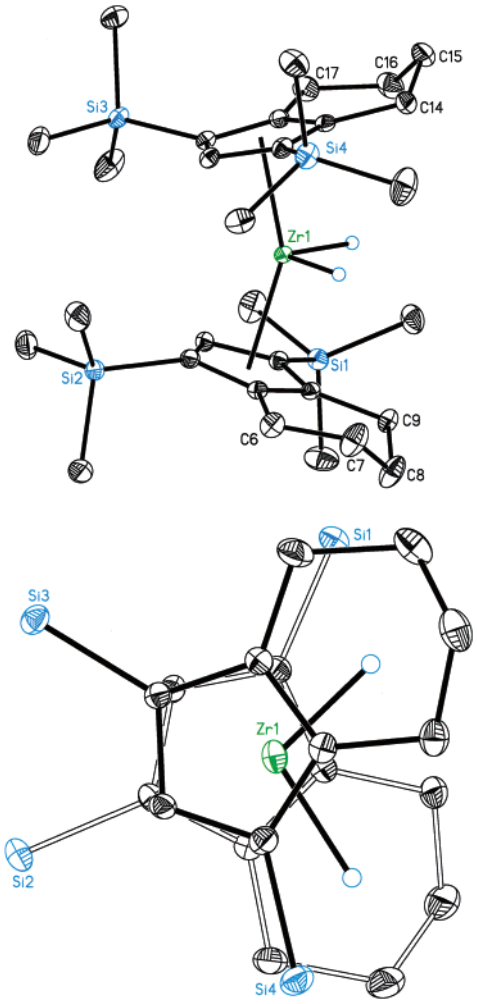


Figure 2. (a) Molecular structure of **1-THI-H$_2$** at 30% probability ellipsoids. (b) Top view of the molecule at 30% probability ellipsoids. Trimethylsilyl substituents and hydrogen atoms, except for the zirconium hydrides, are omitted for clarity.

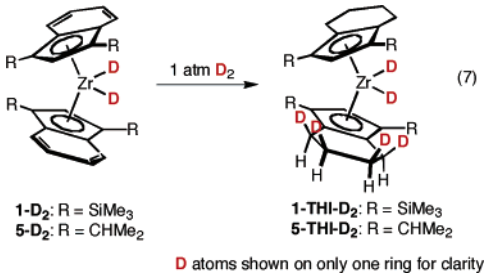
Table 3. Selected Bond Distances and Angles for **1-THI-H$_2$**

Zr(1)−H(1M)	1.85(3) Å
Zr(1)−H(2M)	1.73(3) Å
C(6)−C(7)	1.362(2) Å
C(8)−C(9)	1.371(2) Å
H(1M)−Zr(1)−H(1M′)	101(1)°
rotational angle	79.4(7)°

principal axis bisecting the zirconium−hydride bonds. As a consequence, the indenyl ligands are in a gauche conformation, with a rotational angle of 79.4(7)°. In contrast to **5-H$_2$**, the hydrogenated benzo rings are oriented over the metallocene wedge and serve to block dimerization. The zirconium−hydride bonds were located and refined and have distances of 1.73(3) and 1.85(3) Å. The C−C bond distances in the six-membered rings range between 1.4984(38) and 1.5303(33) Å, consistent with saturated, sp^3-hybridized carbons. By way of comparison, these distances range between 1.362(2) and 1.418(2) Å in **5-H$_2$**. In **1-THI-H$_2$**, deviations between 13.9(1) and 18.3(3)° are observed for the distal tetrahydroindenyl carbons from the idealized plane of the five-membered ring, indicative of a chairlike conformation of the six-membered ring.

Stereochemistry and Mechanism of H$_2$ Addition and Observation of Hydrogenation Intermediates. Because ring hydrogenation at 23 °C was observed by two different synthetic routes, the stereochemistry of hydrogen addition to the benzo group was explored. Additional motivation for this study was provided by the observation of faster rates of benzo ring hydrogenation with the more sterically hindered zirconocene dihydride, **1-H$_2$**. Few studies aimed at understanding the direct interaction of H_2 and bis(indenyl)zirconium compounds have appeared. Pino and co-workers[32] have reported the stereochemistry of PtO_2-catalyzed deuterium addition to *rac*-ethylenebis(indenyl)zirconium dichloride and found that benzo ring hydrogenation (deuteration) occurred exclusively from the exo face of the ligand array.

To explore the possibility of intramolecular ring hydrogenation, **1-D$_2$** was prepared and exposed to additional deuterium gas to achieve complete conversion to **1-THI-D$_2$** (eq 7). As illustrated in the ^{1}H NMR spectrum of **1-THI-D$_2$** presented in Figure 3, the tetrahydroindenyl resonances centered at 2.09 and 2.68 ppm were absent in the isotopically labeled compound. These resonances were directly observed by ^{2}H NMR spectroscopy. On the basis of NOESY NMR experiments, which were used to completely assign the ^{1}H NMR spectrum of **1-THI-H$_2$** (see Supporting Information), deuterium was selectively and exclusively incorporated in the endo positions[33] of the six-membered ring. In contrast to PtO_2-catalyzed benzo ring hydrogenations, where H_2 addition occurs solely from the exo face of the ligand,[32] incorporation of deuterium solely in endo positions is consistent with *intramolecular* ring hydrogenation promoted by **1-H$_2$(D$_2$)**. Endo selectivity was also observed in the deuteration of **5-D$_2$** to **5-THI-D$_2$** (eq 7).



A similar deuterium labeling experiment was conducted with **1-Me$_2$**. Exposure of the dimethyl complex to 1 atm of D_2 gas at 65 °C for 3 days furnished **1-THI-D$_2$**. Analysis of the isotopically labeled zirconocene dihydride by a combination of ^{1}H and ^{2}H NMR spectroscopy established D_2 addition principally from the endo face of the ligand, the same stereochemistry observed from deuteration of the **1-D$_2$**. In this case, substantially more contamination (∼25%) from hydrogen was observed in the endo positions of the deuterated ring. Control experiments involving intermediates in the hydrogenation reaction (vide infra) indicate that cyclometalation of an [SiMe$_3$] group is competitive with ring reduction and serves as a source of hydrogen, rapidly exchanging with the Zr−*D* positions at 65 °C, ultimately placing H- rather than D-atoms in the tetrahydroindenyl ligand.

Rearrangement of Bis(indenyl)zirconium Dihydrides: Isolation of Complexes Bearing η^5,η^3-4,5-Dihydroindenediyl

(32) Waymouth, R. M.; Bangerter, F.; Pino, P. *Inorg. Chem.* **1988**, *27*, 758.
(33) The terms exo and endo refer to the orientation of the hydrogen atoms with respect to the zirconium center. Those directed toward the metal are designated endo, while those pointing away are exo.

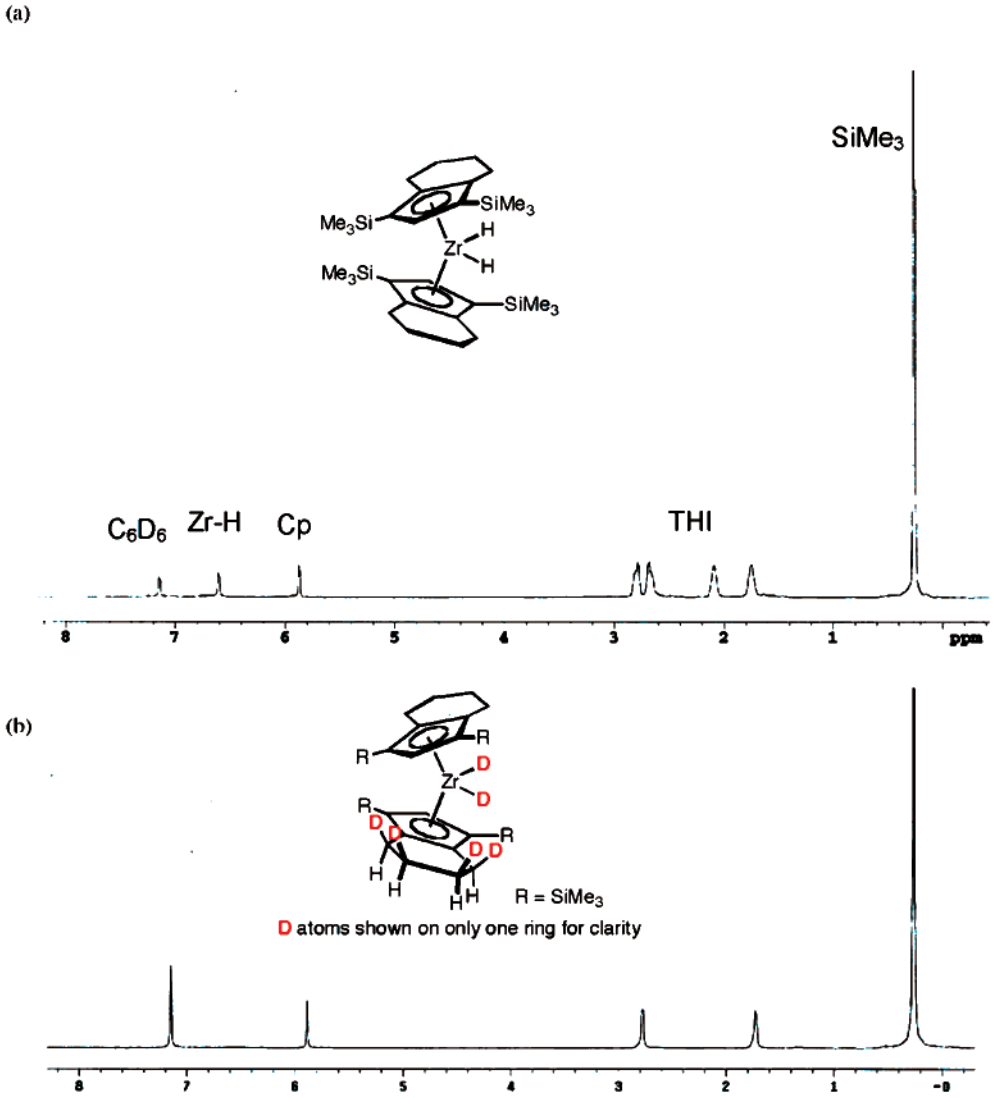
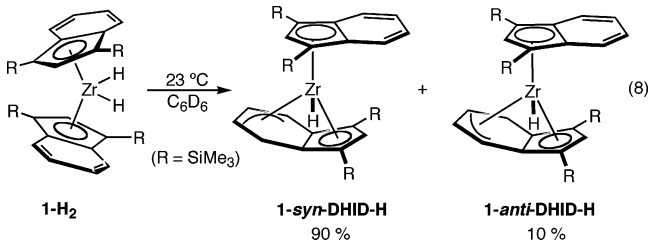


Figure 3. ^{1}H NMR spectra of (a) **1-THI-H$_2$** and (b) **1-THI-D$_2$**.

(DHID) Ligands. Once examples of monomeric bis(indenyl)-zirconocene dihydrides were isolated, the solution stability of this new class of compounds was evaluated. Monitoring a benzene-d_6 solution of **1-H$_2$** at 23 °C by ^{1}H NMR spectroscopy revealed complete consumption of the zirconocene dihydride over the course of 1 h with concomitant growth of two new products (eq 8). If the reaction was performed under vacuum, variable amounts (10−20%) of the η^9,η^5-bis(indenyl)zirconium sandwich compound, **1**, were observed, arising from reductive elimination of dihydrogen from **1-H$_2$**. Observation of this side reaction is in agreement with previous observations of rapid alkane reductive elimination from the corresponding bis-(indenyl)zirconium alkyl hydrides.[24]



The major species, **1-*syn*-DHID-H**, accounts for approximately 90% of the product mixture and has been identified as a coordinatively saturated zirconium hydride complex containing one traditional η^5-indenyl ring and an unusual η^5,η^3-4,5-dihydroindenediyl (DHID) ligand, arising from metal-to-benzo ring hydrogen transfer. The minor product, formed in 10% yield, has been assigned as its stereoisomer, **1-*anti*-DHID-H**, differing only in the disposition of the zirconium hydride and the newly formed methylene carbon in the six-membered ring of the DHID ligand.

Identification of **1-*syn*-DHID-H** was accomplished by a combination of multinuclear and two-dimensional NMR experiments and isotopic labeling studies. In benzene-d_6, the ^{1}H NMR spectrum (Figure 4) of **1-*syn*-DHID-H** exhibits the number of resonances for a C_1-symmetric compound with two different rings. Selected peak assignments are reported in Table 4. In addition to four inequivalent [SiMe$_3$] singlets and typical benzo multiplets in the aromatic region, five multiplets are shifted upfield and have been identified as protons on the six-membered ring of the η^5,η^3-4,5-dihydroindenediyl ligand (Figure 4). The sp^3-hybridized methylene carbon displays exo and endo hydrogens centered at 1.93 and 2.47 ppm, respectively. Furthermore,

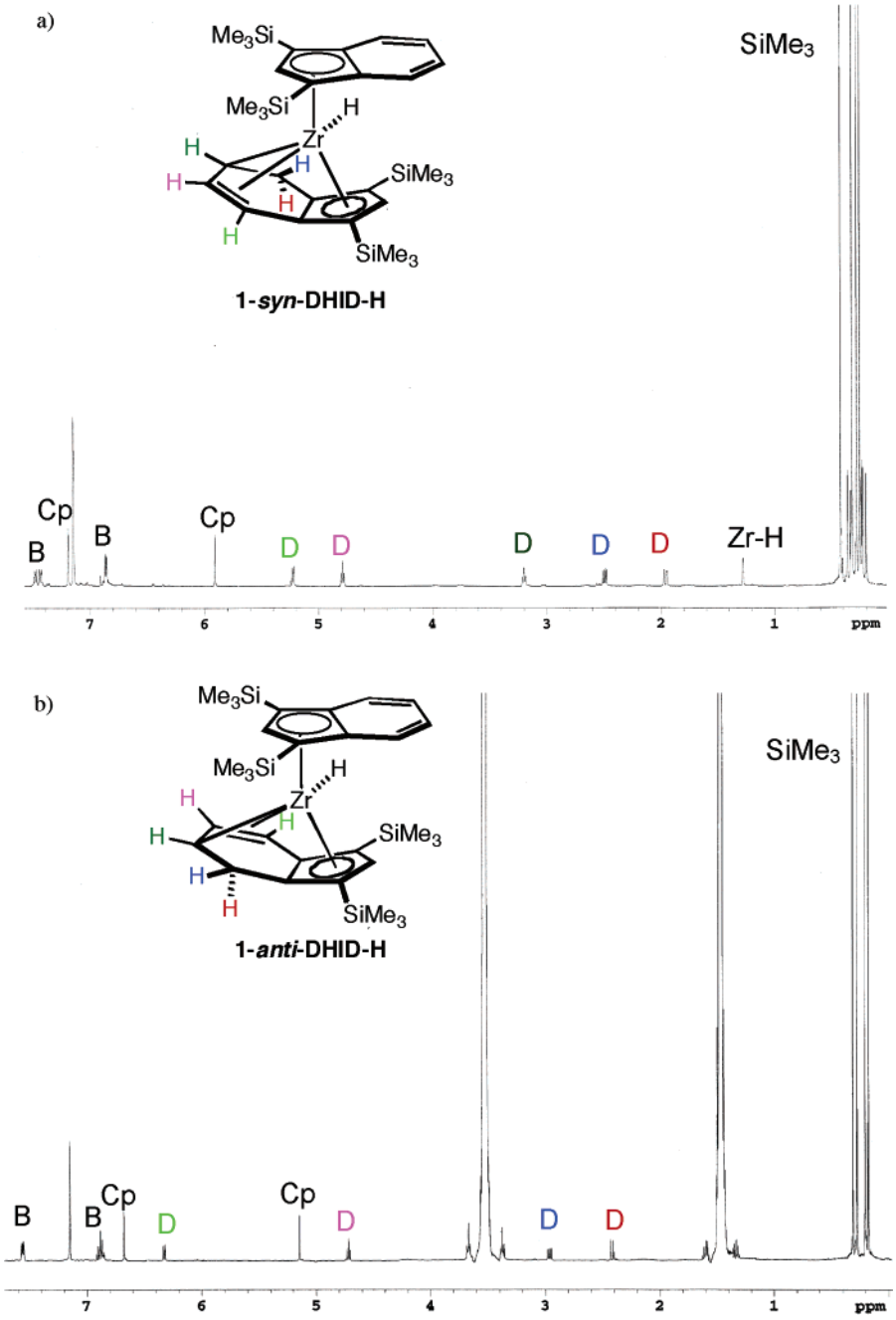


Figure 4. ^{1}H NMR spectra of (a) **1-*syn*-DHID-H** and (b) **1-*anti*-DHID-H** at 23 °C in benzene-d_6. D designates the 4,5-dihydroindenediyl ligand, while B indicates benzo resonances from the indenyl ligand. One DHID resonance and the Zr−*H* resonances are not observed due to peak overlap in **1-*anti*-DHID-H**.

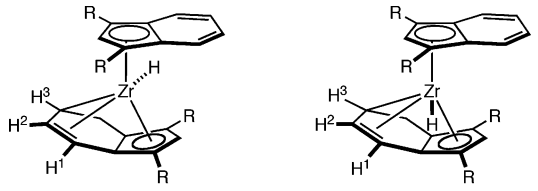
a zirconium−hydride resonance was identified at 1.25 ppm, shifted substantially upfield from the value found in **1-H$_2$**, indicative of a coordinately saturated metal center.[34] NOESY cross-peaks between the zirconium hydride and the endo methylene hydrogen in the six-membered ring establish the stereochemistry of the major isomer as syn, wherein the sp^3-hybridized carbon and the Zr−H are adjacent in the molecule.

Deuterium labeling studies were used to confirm the assignment of the zirconium hydride and the endo methylene hydrogen. Allowing a benzene-d_6 solution of **1-D$_2$** to stand at 23 °C resulted in facile conversion to **1-*syn*-DHID-D**. Notably, the resonances at 1.25 (Zr−*H*) and 2.47 ppm (endo-C*H*$_2$) were absent in the ^{1}H NMR spectrum. These peaks were observed directly by ^{2}H NMR spectroscopy. No evidence for incorporation of deuterium into any other part of the ligands was observed.

The minor isomer, **1-*anti*-DHID-H**, exhibited similar NMR spectral features in benzene-d_6 (Table 4). NOESY spectra and crystallographic studies on a related compound (vide infra) established the anti disposition of the ring methylene hydrogens and the zirconium hydride. For this isomer, the Zr−*H* resonance, identified by deuterium labeling and two-dimensional NMR experiments, appears at 0.33 ppm, significantly upfield-shifted from the syn isomer. The exo and endo methylene hydrogens on the DHID ligand were observed at 2.55 and 3.04 ppm. It is

(34) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309.

Table 4. Selected ^{1}H NMR Chemical Shifts (ppm) of Zirconocene Hydride Complexes Containing η^5,η^3-4,5-Dihydroindenediyl Ligands



1-*syn*-DHID-H: R = $SiMe_3$
2-*syn*-DHID-H: R = $SiMe_2Ph$
5-*syn*-DHID-H: R = $CHMe_2$

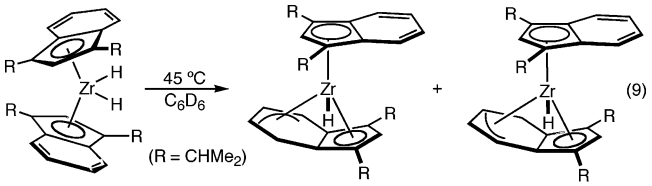
1-*anti*-DHID-H: R = $SiMe_3$
2-*anti*-DHID-H: R = $SiMe_2Ph$
5-*anti*-DHID-H: R = $CHMe_2$

resonance	1-*syn*-DHID-H	2-*syn*-DHID-H	5-*syn*-DHID-H	1-*anti*-DHID-H	2-*anti*-DHID-H	5-*anti*-DHID-H
Zr−H	1.25	1.53	1.81	0.33	0.70	0.92
exo-CH_2[a]	1.93	1.78	2.05	2.55	2.35	2.05
endo-CH_2[a]	2.47	2.46	2.64	3.04	2.95	2.60
H^1	5.21	5.01	4.34	6.44	6.22	6.86
H^2	4.77	4.65	4.34	4.78	4.54	4.56
H^3	3.20	3.22	3.29	1.49	NL[b]	1.35

[a] Refers to the sp^3-hybridized carbon on the η^5,η^3-4,5-dihydroindenediyl ligand. [b] NL = not located.

curious that the relative stereochemistry of the sp^3-hybridized carbon and the zirconium hydride dramatically shifts the resonances for the η^5,η^3-bound ring and the zirconium hydride.

Similar rearrangement chemistry has been observed with the other bis(indenyl)zirconium dihydrides, **2-H_2** and **5-H_2**. Pertinent ^{1}H NMR spectroscopic features are reported in Table 4. The silyl-substituted complex, **2-H_2**, converted at a rate similar to **1-H_2** and also yielded a similar product mixture. For the alkyl-substituted dihydride, **5-H_2**, slow conversion to **5-*syn*-DHID-H** and **5-*anti*-DHID-H** occurred at 23 °C. Complete reaction was observed by warming the solution to 45 °C for 2 days. Significantly, the rearrangement of **5-H_2** to **5-*syn*-DHID-H** was slightly more selective, with **5-*anti*-DHID-H** accounting for less than 5% of the product mixture (eq 9). As with the silylated metallocene, small amounts of **5** were observed upon heating.



5-H_2 **5-*syn*-DHID-H** > 95 % **5-*anti*-DHID-H** < 5 %

The benzene-d_6 solution NMR spectral features of **5-*syn*-DHID-H** are similar to those of **1-*syn*-DHID-H** (Table 4). The zirconium hydride was observed at 1.81 ppm, while the exo and endo protons on the DHID ligand appeared as multiplets centered at 2.05 and 2.64 ppm, respectively. As with **1-*syn*-DHID-H**, the NMR assignments are based on a combination of isotopic labeling studies and two-dimensional experiments.

The solid-state structure of **5-*syn*-DHID-H** was determined by X-ray diffraction and is presented in Figure 5. Selected metrical parameters are reported in Table 5. The data were of sufficient quality that all of the hydrogen atoms, including the zirconium hydride, were located and freely refined. In the solid state, the indenyl rings adopt a nearly gauche conformation with a rotational angle of 82.5(5)°, minimizing transannular steric interactions of the isopropyl substituents. The X-ray data also support the assignment of the syn isomer whereby the zirconium hydride and sp^3-hybridized carbon are proximal.

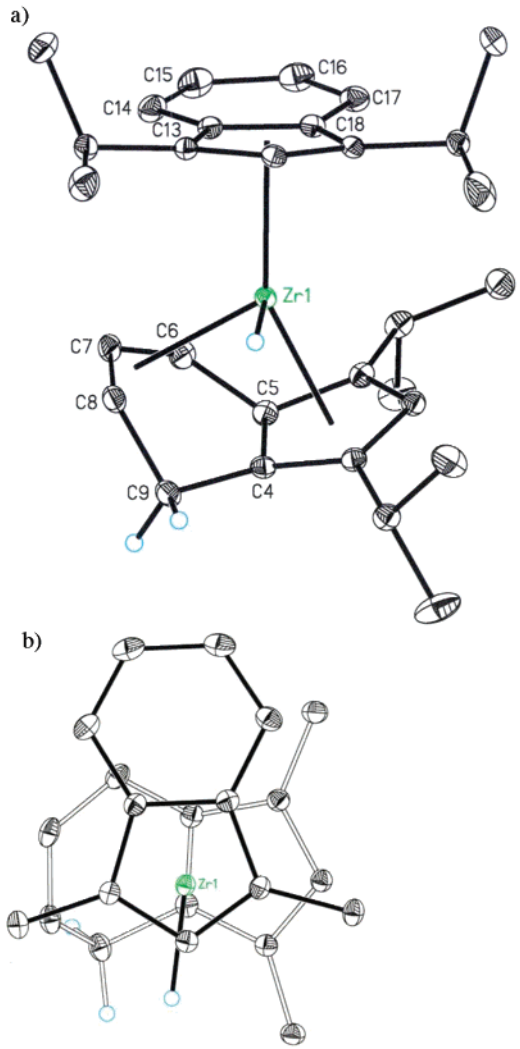


Figure 5. (a) Molecular structure of **5-*syn*-DHID-H** at 30% probability ellipsoids. (b) Top view of the molecule. Isopropyl methyl groups and hydrogen atoms, except for the zirconium hydride and methylene hydrogens, are omitted for clarity.

Hydrogen transfer to the C(9) carbon of the benzo ring is also supported by the metrical data. Both hydrogens were located, and the bond angles are consistent with sp^3 hybridiza-

Table 5. Selected Bond Distances (Å) for **5-*syn*-DHID-H** and **5-*anti*-DHID-H**

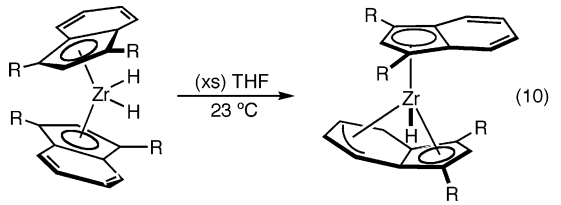
	5-*syn*-DHID-H	5-*anti*-DHID-H
Zr(1)−H(1M)	1.796(17)	1.79(2)
Zr(1)−C(6)	2.4310(13)	2.895(4)
Zr(1)−C(7)	2.4947(12)	2.482(3)
Zr(1)−C(8)	2.5529(13)	2.518(3)
Zr(1)−C(9)	3.054(1)	2.625(4)
C(6)−C(7)	1.4179(18)	1.480(5)
C(7)−C(8)	1.3966(19)	1.398(5)
C(8)−C(9)	1.5142(17)	1.380(5)

tion. The C(4)−C(9) and C(8)−C(9) distances of 1.5185(17) and 1.5142(17) Å are typical for carbon−carbon single bonds and are elongated from distances of 1.36−1.40 Å found in the traditional η^5-indenyl rings in **5-H$_2$**. The Zr(1)−C(8) bond distance of 2.5529(13) Å is slightly elongated compared to the values of 2.4947(12) and 2.4310(13) Å observed for Zr(1)−C(7) and Zr(1)−C(6), respectively, and is within the range found in the analogous benzo carbons of η^9-indenyl ligands.[25] The Zr(1)−C(9) distance of 3.054(1) Å is well outside the sum of the covalent radii and the bond lengths typically found between zirconium and polycyclic aromatic ligands. In addition, the C(9) carbon dips 42.7(1)° below the idealized plane of the other five carbons in the six-membered ring, also consistent with hydrogen transfer.

As was observed in the solid-state structure of η^9-coordinated indenyl ligands,[25] the η^5,η^3-dihydroindenediyl fragment is significantly buckled as a result of coordination to the zirconium center. The "hinge angle" is defined as the angle formed between the planes defined by the five-membered ring and the four sp^2 carbons contained in the six-membered ring. The sp^3 carbon was omitted because of the substantial deviation from the idealized plane. For **5-*syn*-DHID-H**, this value is 44.7(1)°, larger than the buckling found in the corresponding sandwich compound containing an η^9-indenyl ligand,[25] which may be a consequence of the anionic character of the former. To our knowledge, the compounds presented in this work are the first examples of η^5,η^3-4,5-dihydroindenediyl ligands coordinated to a transition metal. Examples of dihydroindene ligands, C_9H_9, have been observed in iron[35] and ruthenium[36] chemistry and are typically prepared from synthetic modification of the corresponding bis(cyclopentadienyl) complex rather than partial reduction of an indenyl ligand.

Because the anti isomers were observed only in low yield from the rearrangement of the bis(indenyl)zirconium dihydrides in benzene-d_6, an alternative synthetic route to the compounds was desired. Our laboratory has previously reported an unusual THF-induced haptotropic rearrangement of one of the indenyl ligands in silyl-substituted η^9,η^5-bis(indenyl)zirconium sandwiches to the corresponding η^6,η^5-bis(indenyl)zirconium THF compounds.[28] As a result, the influence of THF on the stereochemistry of bis(indenyl)zirconium dihydride complexes was investigated. This synthetic protocol was also of interest as the THF complexes, **1-THF** and **2-THF**, are more crystalline and easier to isolate in pure form than more lipophilic **1** and **2**.

Addition of 1 atm of H_2 to a benzene-d_6 solution of **1-THF** with an excess (>50 equiv) of THF present resulted in rapid hydrogenation and subsequent rearrangement to **1-*anti*-DHID-H**. A 1:2 mixture of syn and anti products was observed when no additional THF was present. Attempts to detect the dihydride complex, **1-H$_2$**, or the corresponding THF adduct, **1-H$_2$(THF)**, have been unsuccessful, as isomerization is more rapid than in the absence of THF. The ^{1}H and ^{13}C NMR spectroscopic data indicated exclusive formation of **1-*anti*-DHID-H** (eq 10). Similar observations have been made for the rearrangements of both **2-H$_2$** and **5-H$_2$**. Although **5** does not coordinate THF, addition of approximately 50 equiv of the cyclic ether to **5-H$_2$** provided evidence for **5-H$_2$(THF)** by ^{1}H NMR spectroscopy prior to formation of **5-*anti*-DHID-H**. Notably, the zirconium−hydride resonance shifts upfield to 6.38 ppm in THF-d_8, consistent with an appreciable concentration of a coordinatively saturated zirconocene dihydride. As with **1**, THF catalyzed the selective rearrangement to **5-*anti*-DHID-H** over the course of 2 h at 23 °C (eq 10).



1-H$_2$: R = SiMe$_3$
2-H$_2$: R = SiMe$_2$Ph
5-H$_2$: R = CHMe$_2$

1-*anti*-DHID-H: R = SiMe$_3$
2-*anti*-DHID-H: R = SiMe$_2$Ph
5-*anti*-DHID-H: R = CHMe$_2$

In addition to diagnostic NMR spectral characteristics (Table 4), confirmation of the stereochemistry of **5-*anti*-DHID-H** was accomplished by X-ray diffraction. The solid-state structure is presented in Figure 6, and selected metrical data are reported in Table 5. As anticipated from the solution data, the zirconium hydride is directed away from the sp^3-hybridized carbon, C(6), opposite of the configuration observed in the solid-state structure of **5-*syn*-DHID-H**. The zirconium−carbon distances in the η^3 portion of the benzo ring are slightly elongated from the syn isomer, ranging between 2.482(3) and 2.625(4) Å. Accordingly, the nonbonded carbon in the benzo ring is slightly closer to the metal at 2.895(4) Å, as compared to the distance of 3.054(1) Å for the syn. The hinge angle, as defined for the syn isomer, is 44.5(1)°, indicative of a substantial distortion from planarity. Likewise, the methylene carbon is distorted 39.6(2)° from the idealized plane defined by the remaining carbons in the six-membered ring of **5-*anti*-DHID-H**.

Mechanism of Dihydride Rearrangement. The observation of the rearrangement of bis(indenyl)zirconocene dihydrides to complexes containing η^5,η^3-4,5-dihydroindenediyl ligands and the unusual influence of THF on the rate and stereochemical outcome of the reaction prompted investigation into the mechanism of isomerization. Two possible mechanisms are proposed in Figure 7. For the following discussion, **1-H$_2$** will be used as a representative example of a bis(indenyl)zirconium dihydride.

The first pathway involves insertion of the C═C bond of the benzo ring into the zirconium−hydride in analogy to well-established hydrozirconation reactions.[37] An alternative mechanism involves reversible reductive elimination of H_2 from **1-H$_2$**, regenerating **1**. The liberated H_2 then adds across the zirconium−

(35) (a) Izumi, T.; Tamura, F.; Sasaki, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2784. (b) Trainor, G. L.; Breslow, R. *J. Am. Chem. Soc.* **1981**, *103*, 154.
(36) Hofer, O.; Schlögl, K. *Tetrahedron Lett.* **1967**, *36*, 3485.
(37) Labinger, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Chapter 3.9.

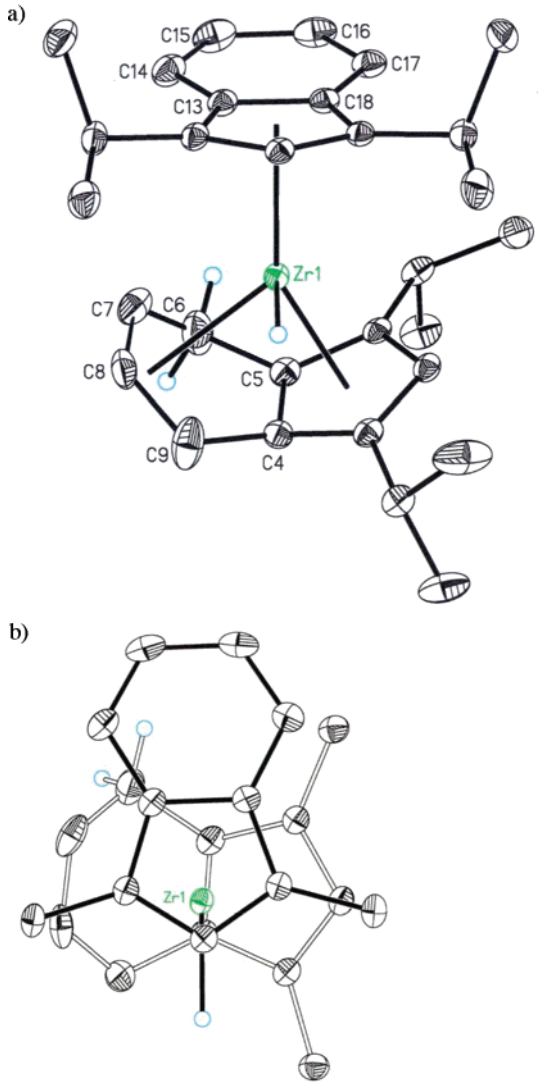


Figure 6. (a) Molecular structure of **5-*anti*-DHID-H** at 30% probability ellipsoids. (b) Top view of the molecule. Isopropyl methyl groups and hydrogen atoms, except for the zirconium hydride and methylene hydrogens, are omitted for clarity.

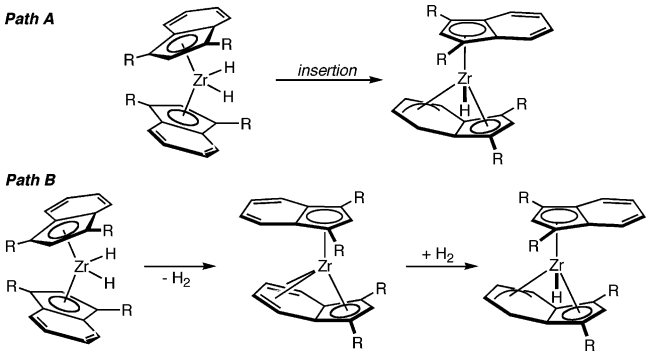
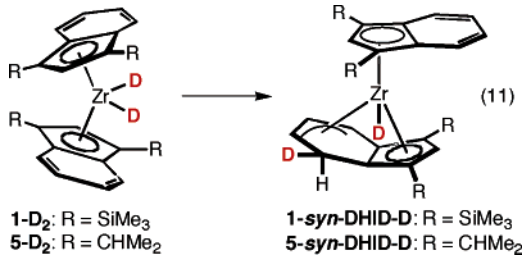


Figure 7. Possible mechanisms for the formation of η^5,η^3-4,5-dihydroindenediyl ligands from the corresponding dihydrides.

carbon bond of the η^9 ring. If operative, this mechanism suggests that the bis(indenyl)zirconocene dihydrides are merely byproducts and not intermediates to the rearranged complexes. This pathway would also account for the observation of trace amounts of sandwich compounds observed during rearrangement.

A series of experiments were conducted in an attempt to distinguish between the two proposed pathways. As presented above, rearrangement of bis(indenyl)zirconocene dideuterides, **1-D$_2$** and **5-D$_2$**, selectively places the deuterium in the endo position of the methylene carbon (eq 11). Unfortunately, stereoselective deuteration of this position is consistent with both proposed mechanisms, as both the hydrogenolysis and the insertion pathways are expected to yield the observed products.



The relative rates of isomerization are also not useful in distinguishing between the two mechanistic possibilities. In the absence of THF, **1-H$_2$** rearranges faster than **5-H$_2$**. If insertion were operative, this result would be expected, as the rate of cyclohexene insertion with **1-H$_2$** is faster than that for **5-H$_2$**, a consequence of the increased electrophilicity of the silyl-substituted zirconocene.[38] A similar trend is expected for the reductive elimination pathway, as previous studies have established that silylated zirconocenes undergo reductive elimination faster than their alkylated counterparts.[39]

A normal, primary kinetic isotope effect, $k_H/k_D = 1.7(3)$, has been measured at 23 °C for the isomerization of **1-H$_2$(D$_2$)** to **1-*syn*-DHID-H(D)**. The determination was made by monitoring the conversion of zirconocene dihydride to the product in parallel NMR tubes. An effect of this direction and magnitude is similar to the values reported for olefin insertion with zirconocene dihydrides (dideuterides)[20] and is consistent with an insertion pathway. However, it should be noted that a similar value could be expected for the mechanism presented in Path B: the overall transformation is a composite of reductive coupling, H_2 loss, and hydrogenolysis of metal−carbon bonds. Because the rate-determining step is unknown, the observed kinetic isotope, potentially being a composite of these individual transformations, does not alone distinguish this mechanism from Path A.

In principle, performing the isomerization reaction under conditions where dihydrogen could be removed as it is formed could possibly distinguish the different mechanistic pathways. If reductive elimination were operative, performing the isomerization reaction under a vacuum should ideally lead to exclusive formation of the η^9,η^5-bis(indenyl)zirconium sandwich rather than the rearranged product. Allowing **1-H$_2$** to stand in benzene-d_6 at 23 °C under vacuum furnished an equilibrium mixture of **1-*syn*-DHID-H** and **1-*anti*-DHID-H**, essentially in the same ratio as in the presence of N_2. The same ratio was also obtained regardless of whether the reaction was carried out with approximately 1 mL of headspace in a sealed NMR tube or with 300 mL in a glass vessel. Performing the same reaction in a large volume of toluene under constant dynamic vacuum also yielded the rearranged products. In this experiment, small (∼20%) quantities of **1** were observed, most likely arising from competitive (vide infra) reductive elimination of H_2.

(38) Bradley, C. A.; Keresztes, I.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 2080.
(39) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241.

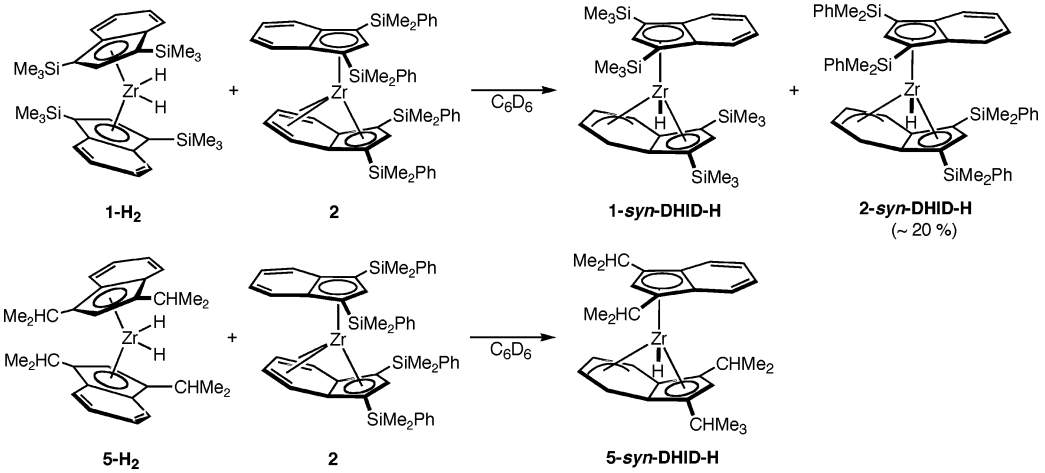


Figure 8. Crossover experiments conducted with bis(indenyl)zirconocene dihydrides.

The experiments conducted under vacuum, while not conclusively excluding the reductive elimination pathway, support insertion. To gain additional experimental evidence for this possibility, a series of crossover experiments were conducted. Mixing equimolar quantities of **1-H$_2$** and **2** resulted in nearly quantitative formation of the rearranged products derived from **1** (Figure 8). Small amounts (~20%) of **2-*syn*-DHID-H** were detected and most likely arise from competitive reductive elimination of H_2 to form **2-H$_2$**, which undergoes subsequent rearrangement. If reductive elimination were the sole pathway operative, a statistical mixture of the two different rearranged products would be expected. In a related experiment, **5-H$_2$** was mixed with **2**, and **5-*syn*-DHID-H** was formed exclusively. In this case, it is important to note that **2** reacts with H_2 much faster than **5**, and if reductive elimination to form free dihydrogen were operative, significant quantities of **2-H$_2$** (or its rearranged products) would be expected. Control experiments, whereby mixtures of bis(indenyl)zirconocene dihydrides and deuterides of **1**, **2**, and **5** were prepared and produced little isotopic exchange, ruled out dimerization through formation of hydride bridges.

On the basis of the experimental data, the hydride rearrangements most likely proceed via an intramolecular olefin insertion process. The absence of significant crossover during the rearrangement of **1-H$_2$** and **5-H$_2$** offers the strongest evidence in support this assertion. The observation of trace crossover with **1-H$_2$** and not **5-H$_2$** is a result of the relative rates of reductive elimination in the case where the more electrophilic silyl-substituted zirconocenes undergo more facile reductive elimination than their alkylated counterparts. In addition, the observation of two stereoisomers from rearrangement also argues against a reductive elimination−hydrogenolysis mechanism, particularly since formation of **1-*anti*-DHID-H** requires a trans addition of H_2 across the zirconium−carbon bond. While exclusive formation of the syn isomer followed by isomerization could possibly account for the second stereoisomer, such a process would require a different mechanism for isomerization and, as will be presented below, contrasts the thermodynamic preference for the syn isomer. The preferred insertion mechanism entails precoordination of a benzo C=C bond to the zirconium, requiring a distortion from planarity. While it may seem unlikely that a conjugated carbocycle like indenyl would bend, crystallographic characterization of η^9-hapticity provides precedent for the geometric flexibility of this ligand class.[25]

Although the insertion mechanism seems plausible and is in agreement with the experimental data, questions remain about the influence of THF on both the stereochemistry and the rate of rearrangement. Specifically, why does the insertion yield predominantly syn products in non-coordinating solvents such as pentane and benzene yet produce the anti isomer in the presence of THF? Perhaps more difficult to reconcile is the rate enhancement observed upon addition of a coordinating Lewis base.

Several experiments were conducted in an attempt to address these issues. One possibility was that the observed differences were a result of solvent polarity rather than coordination effects. To probe this possibility, the rearrangement of **1-H$_2$** was independently carried out in the presence of a large excess (~50 equiv) of THF and 2,5-dimethyl-THF. Bergman has previously established that the two solvents have similar polarities but vastly different coordination abilities.[40] Rearrangement in the presence of 2,5-dimethyl-THF proceeded with the same selectivity as in benzene-d_6, demonstrating that the observed rate and stereochemical differences are a result of THF coordination rather than a change in polarity of the medium. Similarly, performing the rearrangement of **1-H$_2$** in the presence of a large excess of diethyl ether also produced the same outcome as the reaction in neat benzene-d_6.

Because THF coordination appears to be the origin of the differences observed in the isomerization reactions, ligand adducts of the bis(indenyl)zirconocene dihydride complexes were studied in more detail. For **1-H$_2$**, a discrete THF adduct of the dihydride compound has not been observed due to the rapid rate of conversion to **1-*anti*-DHID-H**. In the case of **5-H$_2$**, where the rate of rearrangement is slower, addition of a large excess of THF produced an upfield shifting of the hydride resonance, consistent with formation of **5-H$_2$(THF)**. Because the rearrangement of **5-H$_2$**/**5-H$_2$(THF)** was relatively slow at 23 °C, the rate of isomerization as a function of THF concentration was determined. Performing the conversion of **5-H$_2$** to **5-*anti*-DHID-H** in benzene-d_6 in the presence of 50 equiv of THF produced an observed first-order rate constant of $1.7(1) \times 10^{-4}$ s^{-1}. This value increases to $2.5(1) \times 10^{-4}$ s^{-1} upon increasing the THF concentration to 75 equiv. At 100 equiv, the observed rate constant is $2.7(1) \times 10^{-4}$ s^{-1},

(40) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

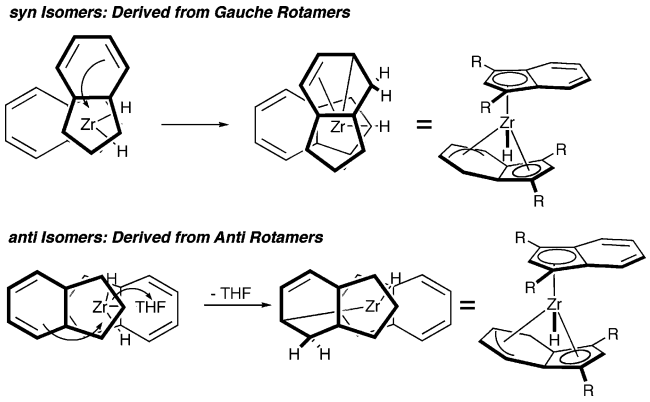


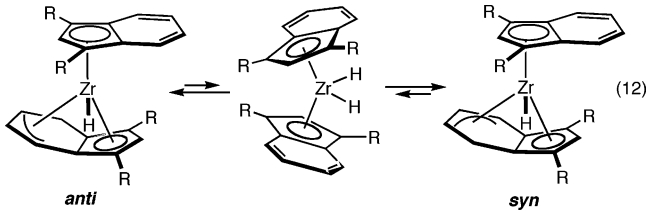
Figure 9. Origin of syn versus anti isomers in the rearrangement of bis-(indenyl)zirconium dihydride complexes. Indenyl substituents are omitted for clarity.

statistically invariant from the value at 75 equiv, suggesting saturation has been achieved.

Concurrent with the studies reported here, our laboratory has also been exploring the chemistry of other ligand adducts of bis(indenyl)zirconocene dihydrides. Addition of PMe_3 to both **1-H$_2$** and **5-H$_2$** yielded isolable phosphine hydride complexes, (η^5-C_9H_5-1,3-R_2)$_2$ZrH_2(PMe_3) (R = $SiMe_3$, **1-H$_2$(PMe$_3$)**; $CHMe_2$, **5-H$_2$(PMe$_3$)**).[38] NMR spectroscopic characterization of both complexes in solution, in combination with the solid-state structure of **5-H$_2$(PMe$_3$)**, established that coordination of the phosphine ligand induced a change in indenyl ligand conformation. In contrast to the solid-state structure of **5-H$_2$**, where essentially gauche rings are observed, the phosphine dihydride complexes contain nearly anti indenyl rings with one benzo substituent oriented directly over the metallocene wedge (Table 2). Another difference between the two structures is the "tilt" of the indenyl ligands away from the zirconocene hydride positions. The values for both the interplanar ring angle (α) and the β parameter (Table 2) demonstrate a significant bending of the ligands "back" upon coordination of PMe_3. Despite these structural differences, only a slight deviation from η^5-hapticity is observed in the metrical parameters, far from the accepted values typically ascribed to η^3-coordination.

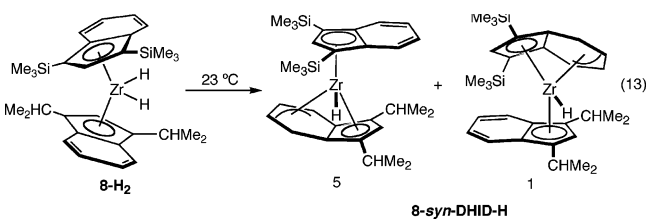
These conformational changes are likely the origin of the divergent stereochemistries observed in the presence versus in the absence of THF. As presented in Figure 9, syn isomers are obtained from coordination of the benzo C=C bond to the lateral position of the metallocene wedge. Preference for the gauche isomer in the absence of THF places the incipient C=C bond directly over the lateral coordination site, in proximity to the $1a_1$ orbital of the zirconocene.[41] In contrast, anti products can result from two different trajectories derived from the anti rotamer. Approach of the C=C bond from the benzo ring over the metallocene wedge leads to coordination between the two zirconium hydrides, maintaining mirror plane symmetry. An alternative pathway involves backside attack of the C=C bond of the opposite benzo ring on the zirconium center, resulting in olefin coordination in the lateral position of the metallocene wedge. This trajectory may also be favored by the increased bending of the indenyl ligands away from the metallocene wedge observed upon ligand complexation (Table 2). While ligand coordination in the central position is thermodynamically preferred, insertion reactions from the lateral sites are believed to be more facile.[41,42] This latter pathway may also account for the observed rate enhancement and suggests the importance of a pre-equilibrium involving the zirconocene dihydride and the corresponding THF adduct. THF coordination would place the indenyl rings in a preferred arrangement for an interchange associative attack on the zirconium center. However, based on the experimental data available, this conclusion is tenuous and should be treated with caution, as slippage to η^3 intermediates along the reaction coordinate and other possibilities have not been excluded.

When both stereoisomers of the rearranged products were isolated, the relative thermodynamic stabilities of the two isomers were determined. Removing the THF from benzene-d_6 solutions of the pure anti isomers resulted in conversion to the corresponding syn compound over the course of hours at 23 °C (eq 12). Likewise, addition of an excess of THF to a 9:1 mixture of **1-*syn*-DHID-H** to **1-*anti*-DHID-H** produced no change. According to the principle of microscopic reversibility, the mechanism for conversion of the anti to the syn isomer proceeds by β-hydrogen elimination[43] to generate the zirconocene dihydride complex, followed by reinsertion. The observed isomer preference in the absence of THF supports the conformational argument, where gauche rotamers lead to syn rearranged products arising from lateral insertion.



(12)

To gain further insight into the kinetic and mechanistic preferences for hydrogen transfer to the benzo ring of the indenyl ligand, a mixed alkyl−silyl bis(indenyl)zirconium dihydride was synthesized. Addition of 1 atm of H_2 to (η^9-C_9H_5-1,3-($CHMe_2$)$_2$)-(η^5-C_9H_5-1,3-($SiMe_3$)$_2$)Zr (**8**)[25] furnished the corresponding dihydride complex, **8-H$_2$**. At 23 °C, hydride rearrangement afforded a 5:1 mixture of two isomers of **8-*syn*-DHID-H** (eq 13). Allowing the solution to stand at ambient temperature for 24 h produced no change, suggesting that the mixture was at equilibrium. A combination of two-dimensional NMR experiments allowed assignment of the major isomer as the one arising from hydride transfer to the alkylated indenyl ligand while the minor is the opposite case, where the sp^3-hybridized carbon is on the silylated indenyl ring.

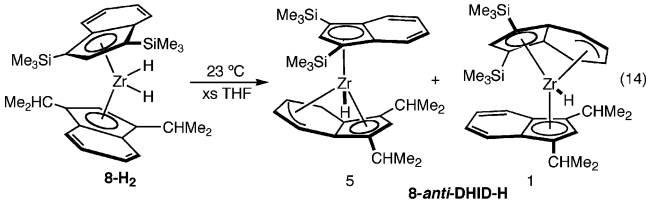


(13)

The stereochemistry of the isomerization of **8-H$_2$** was also studied in the presence of a large excess (~50 equiv) of THF.

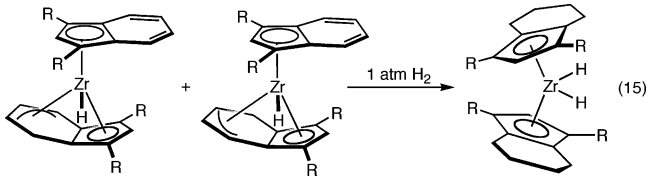
(41) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.
(42) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 608.
(43) Because β-hydrogen elimination occurs from formally coordinatively saturated compounds, opening of a coordination site either through ring slippage or olefin dissociation is likely.

At 23 °C, a 5:1 mixture of two isomers of **8-*anti*-DHID-H** were observed after 3 min. The ratio of products remains unchanged upon the solution standing at ambient temperature for 3 h. As with the syn isomer, two-dimensional NMR experiments established a preference for hydrogen transfer to the alkylated rather than silylated indenyl ring (eq 14). This preference is opposite to that observed for ligand-induced haptotropic rearrangement, where silylated indenyls are more likely to adopt η^6-hapticity.[28]



The observed preference for hydrogen transfer to the alkylated rather than the silyl ring in the rearrangement to both syn and anti products is most likely a result of the more electron rich and hence nucleophilic olefin arising from isopropyl substitution. The different steric environments of the two ligands also likely play a role. While **1-H$_2$** undergoes rearrangement faster than **5-H$_2$**, the insertion of the alkylated ring at ambient temperature suggests that the silylated indenyl ring imparts a sufficiently electrophilic zirconium center to favor rearrangement at 23 °C. Thus, the two rings work in concert to provide the observed selectivity.

The Intermediacy of η^5,η^3-4,5-Dihydroindenediyl Ligands in Hydrogenation to Tetrahydroindenyl Derivatives. The possible intermediacy of the η^5,η^3-4,5-dihydroindenediyl ligands in the hydrogenation of indenyl rings to the corresponding tetrahydroindenyl derivatives was explored. Treatment of either isomer of **1-DHID-H** or **5-DHID-H** with 1 atm of H_2 resulted in hydrogenation of both rings to furnish **1-THI-H$_2$** and **5-THI-H$_2$**, respectively (eq 15). These results account for the observation of endo deuterium incorporation in the preparation of tetrahydroindenyl complexes and implicate η^5,η^3-4,5-dihydroindenediyl ligands and subsequent hydrogenated products as key intermediates in the addition of H_2 to indenyl ligands.



Concluding Remarks

Oxidative addition of dihydrogen to η^9,η^5-bis(indenyl)-zirconium sandwich compounds has provided a convenient synthetic route to bis(indenyl)zirconocene dihydrides, where the unsaturation of the benzo substituents remains intact. In the absence of H_2, the C=C bond of the benzo substituents undergoes regio- and essentially stereospecific insertion into one of the zirconium−hydride bonds, providing the first examples of η^5,η^3-4,5-dihydroindenediyl ligands. The stereochemistry of the insertion reaction and hence the resulting zirconocene monohydride product is dictated by the preferred conformation of the indenyl rings. In the absence of donor ligands, crystallographic studies have established a preference for gauche rotamers, which ultimately leads to syn-rearranged products. The presence of σ-donating ligand such as THF favors formation of the anti rotamer, leading to the anti isomer. Isomerization of the anti to the syn compound occurs through β-hydrogen elimination and establishes the thermodynamic preference for the syn isomer at ambient temperature. Both stereoisomers of the η^5,η^3-4,5-dihydroindenediyl products undergo further hydrogenation to the corresponding tetrahydroindenyl derivatives, consistent with intramolecular insertion events being responsible for benzo ring hydrogenation.

Experimental Section[44]

Preparation of (η^5-C$_9$H$_5$-1,3-(CHMe$_2$)$_2$)$_2$ZrH$_2$ (5-H$_2$). A thick-walled glass vessel was charged with 0.145 g (0.300 mmol) of **5**, and approximately 5 mL of pentane was added. The vessel was submerged in liquid nitrogen, the contents were evacuated, and 1 atm of dihydrogen was admitted. The vessel was then quickly warmed to ambient temperature and stirred until a color change to yellow occurred. The vessel was again submerged in liquid nitrogen, and the volatiles were removed in vacuo. Solvent removal, followed by recrystallization from pentane at −35 °C, afforded 0.091 g (63%) of a yellow solid identified as **5-H$_2$**. Anal. Calcd for $C_{30}H_{40}Zr$: C, 73.26; H, 8.20. Found: C, 73.17; H, 7.93. ^{1}H NMR (benzene-d_6): δ = 1.12 (d, J = 7 Hz, 12H, CHMe_2), 1.17 (d, J = 7 Hz, 12H, CHMe_2), 2.77 (m, 4H, CHMe$_2$), 6.79 (m, 4H, Benzo), 6.86 (s, 2H, Zr−H), 6.97 (m, 4H, Benzo), 7.68 (s, 2H, Cp). ^{13}C NMR (benzene-d_6): δ = 22.11, 26.43, 26.51 (CHMe$_2$), 109.98 (Cp), 121.95, 122.11, 122.55, 125.55 (Cp/Benzo). IR (pentane): ν_{Zr-H} = 1465 cm^{-1}; ν_{Zr-D} = 1068 cm^{-1}.

Preparation of (η^5-C$_9$H$_9$-1,3-(SiMe$_3$)$_2$)$_2$ZrH$_2$ (1-THI-H$_2$). A thick-walled glass vessel was charged with 0.340 g (0.560 mmol) of **1**, and 5 mL of toluene was added. The vessel was sealed, removed from the drybox, frozen in liquid nitrogen, and degassed on a vacuum line. One atmosphere of hydrogen was then added to the reaction at liquid nitrogen temperature. The reaction mixture was warmed to room temperature and stirred for 12 h at 60 °C. After this time, the volatiles were removed on a vacuum line, and subsequent recrystallization from pentane at −35 °C yielded 0.166 g (48%) of an off-white solid identified as **1-THI-H$_2$**. Anal. Calcd for $C_{30}H_{56}Si_4Zr$: C, 58.08; H, 9.10. Found: C, 58.45; H, 8.85. ^{1}H NMR (benzene-d_6): δ = 0.27 (s, 36H, SiMe_3), 1.75 (br, 4H, THI), 2.09 (br, 4H, THI), 2.68 (br, 4H, THI), 2.79 (br, 4H, THI), 5.88 (s, 2H, Cp), 6.61 (s, 2H, Zr−H). ^{13}C NMR (benzene-d_6): δ = 1.73 (SiMe_3), 24.47, 28.42 (THI), 113.40, 118.42, 138.57 (Cp).

Preparation of (η^5-C$_9$H$_5$-1,3-(CHMe$_2$)$_2$)(η^5,η^3-C$_9$H$_6$-1,3-(CHMe$_2$)$_2$)-ZrH (5-*syn*-DHID-H). A thick-walled glass vessel was charged with 0.150 g (0.310 mmol) of **5** and approximately 10 mL of toluene. The vessel was removed from the drybox, frozen in liquid nitrogen, and evacuated on a high-vacuum line. Dihydrogen was added to the vessel, and the reaction mixture was subsequently warmed to ambient temperature and stirred for 15 min. After this time, the reaction mixture was again frozen in liquid nitrogen and the vessel evacuated. Upon thawing, the vessel was heated in a 45 °C oil bath for 3 days. Solvent removal in vacuo, followed by recrystallization from pentane, yields 0.048 g (32%) of **5-*syn*-DHID-H** as a yellow solid. Anal. Calcd for $C_{30}H_{50}Zr$: C, 73.26; H, 8.20. Found: C, 73.25; H, 8.19. ^{1}H NMR (benzene-d_6): δ = 1.00 (br, 6H, 2CHMe_2), 1.05 (d, J = 8 Hz, 3H, CHMe_2), 1.12 (d, J = 8 Hz, 3H, CHMe_2), 1.25 (d, J = 8 Hz, 3H, CHMe_2), 1.37 (d, J = 8 Hz, 3H, CHMe_2), 1.48 (d, J = 8 Hz, 3H, CHMe_2), 1.54 (d, J = 8 Hz, 3H, CHMe_2), 1.81 (s, 1H, Zr−H), 2.05 (d, J = 10 Hz, 1H, CH_2), 2.19 (m, 1H, CHMe$_2$), 2.52 (m, 1H, CHMe$_2$), 2.64 (m, 1H, allyl CH), 3.01 (m, 1H, CHMe$_2$), 3.18 (m, 1H, CHMe$_2$), 3.29 (br, 1H, allyl CH), 4.34 (br, 1H, allyl CH), 4.35 (br, 1H, allyl

(44) General considerations and additional experimental procedures are contained in the Supporting Information.

C*H*), 5.42 (s, 1H, Cp), 6.76 (m, 1H, Benzo), 6.86 (s, 1H, Cp), 6.93 (m, 1H, Benzo), 6.99 (d, $J = 8$ Hz, 1H, Benzo), 7.24 (d, $J = 8$ Hz, 1H, Benzo). ^{13}C NMR (benzene-d_6): $\delta = 20.85$, 21.69, 21.82, 22.82, 23.92, 24.46, 26.20, 26.43, 27.40, 27.87, 27.90, 28.33, 28.99 ($CHMe_2$/CH_2), 46.07, 89.30, 100.92, 102.34, 106.10, 112.15, 115.03, 116.09, 117.63, 118.14, 120.83, 120.93, 121.11, 121.63, 122.92, 122.98, 125.29 (Cp/Benzo).

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Supporting Information Available: Additional experimental procedures, detailed NMR spectral characterization, and selected kinetic data (PDF); crystallographic data for **5-H$_2$**, **1-THI-H$_2$**, **5-*syn*-DHID-H**, and **5-*anti*-DHID-H** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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