Bis(indenyl)hafnium Chemistry: Ligand-Induced Haptotropic Rearrangement and Fundamental Reactivity Studies at a Reduced Hafnium Center

Doris Pun, Scott M. Leopold, Christopher A. Bradley, Emil Lobkovsky, and Paul J. Chirik*

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853

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The chemistry of reduced bis(indenyl)hafnium compounds has been explored. Sodium amalgam reduction of (η^5-C_9H_5-1,3-$(SiMe_3)_2)_2HfCl_2$ was studied in several different solvents. While reduction in toluene resulted in decomposition, performing the reaction in the presence of THF or 1,2-dimethoxyethane (DME) yielded η^6,η^5-bis(indenyl)hafnium solvent (THF or DME) complexes arising from ligand-induced haptotropic rearrangement. Using less coordinating solvents such as diethyl ether or 2,5-dimethyl THF furnished a rare example of a structurally characterized hafnocene(III) complex, (η^5-C_9H_5-1,3-$(SiMe_3)_2)_2HfCl$. An unusual sodium chloride complex of η^6,η^5-bis(indenyl)hafnium, [(η^6-C_9H_5-1,3-$(SiMe_3)_2$)(η^5-C_9H_5-1,3,-$(SiMe_3)_2)HfCl]_2Na[Na(DME)_3]$, was also isolated and crystallographically characterized as a byproduct from synthesis of the DME compound. The reactivity of the η^6,η^5-bis(indenyl)hafnium THF compound as an isolable source of Hf(II) was also evaluated. Addition of H_2 or *N*,*N*-dimethylaminopyridine (DMAP) resulted in facile oxidative addition, while C−O cleavage of THF was observed upon mild heating. Preparation of the corresponding hafnocene dicarbonyl derivatives allowed comparison of the electronic properties of the new complexes as compared to their zirconocene congeners.

Introduction

The chemistry of reduced bis(cyclopentadienyl) group 4 transition metal complexes has attracted continued attention since Wilkinson's seminal studies of metal sandwich complexes.[1,2] Applications range from two-electron reducing agents for organic synthesis[3] to N_2-fixing complexes that yield ammonia upon hydrogenation[4] and nitrogen-containing organic molecules when treated with the appropriate carbon sources.[5−9]

Within the group 4 triad, divalent bis(cyclopentadienyl)titanium compounds are the most prevalent.[10] Seminal reports from Bercaw and Brintzinger described the solution characterization of (η^5-$C_5Me_5)_2Ti$,[11] a molecule that has thus far eluded isolation in the solid state. Increasing the size of one of the cyclopentadienyl substituents has produced an array of isolable titanocenes and resulted in the structural characterization of a family of (η^5-$C_5Me_4R)_2Ti$ (R = silyl, alkyl) complexes.[12−14] Observation or isolation of a bis(cyclopentadienyl)zirconium or hafnium sandwich complex has proven more challenging, as competing reactions such as cyclopentadienyl substituent cyclometalation[15] are rapid and provide kinetically facile routes to the thermodynamically preferred highest oxidation state.

Replacing the cyclopentadienyl rings with 1,3-disubstituted indenyl ligands has provided a wealth of reduced zirconium chemistry. For example, sodium amalgam reduction of (η^5-C_9H_5-1,3-$R_2)_2ZrCl_2$ complexes bearing relatively large substituents (e.g., R = $CHMe_2$, $SiMe_3$, $SiMe_2{}^tBu$) has resulted in isolation of the bis(indenyl)zirconium sandwich complexes. Instead of a traditional η^5,η^5 linear metallocene, one of the indenyl ligands is significantly buckled due to η^9-coordination, where all nine carbons are bound to the metal center.[16] Both NMR spectroscopic[16] and computational studies[17] established facile and reversible dissociation of the coordinated benzo rings in benzene solution at 23 °C, providing access to the putative η^5,η^5-bis(indenyl)zirconium sandwich, the indenyl version of the long sought after "zirconocene".

Reducing the size of the indenyl substituents to a combination of methyl and isopropyl groups has resulted in the synthesis of activated, end-on dinitrogen complexes with inclusion of NaCl (Figure 1).[18] Similar substituent effects were observed in mixed pentamethylcyclopentadienyl (Cp*), indenyl complexes where

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* Corresponding author. E-mail: pc92@cornell.edu.

(1) Cotton, F. A. *J. Organomet. Chem.* **2001**, *637*, 18.

(2) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281.

(3) *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, 2002, and references therein.

(4) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.

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

(6) Morello, L.; Love, J. B.; Patrick, B. O.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2004**, *126*, 9480.

(7) Knobloch, D. J.; Toomey, H. E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 4248.

(8) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2858.

(9) Bernskoetter, W. H.; Olmos, A. V.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10696.

(10) Chirik, P. J.; Bouwkamp, M. W. *Comprehensive Organometallic Chemistry III*.

(11) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2045.

(12) Hitchcock, P. B.; Kerton, F. M.; Lawless, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 10264.

(13) (a) Lukesová, L.; Horácek, M.; Stepnicka, P.; Fejfarová, K.; Gyepes, R.; Cisorová, I.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2002**, *663*, 134. (b) Horacek, M.; Kupfer, V.; Thewalt, U.; Stepnicka, P.; Polasek, M.; Mach, K. *Organometallics* **1999**, *18*, 3572.

(14) Hanna, T. E.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14688.

(15) Horácek, M.; Stepnicka, P.; Kubista, J.; Fejfarová, K.; Gyepes, R.; Mach, K. *Organometallics* **2003**, *22*, 861.

(16) Bradley, C. A.; Keresztes, I.; Lobkovsky, E.; Young, V. G.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16937.

(17) Veiros, L. F. *Chem.−Eur. J.* **2005**, *11*, 2505.

(18) Pun, D.; Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 14046.

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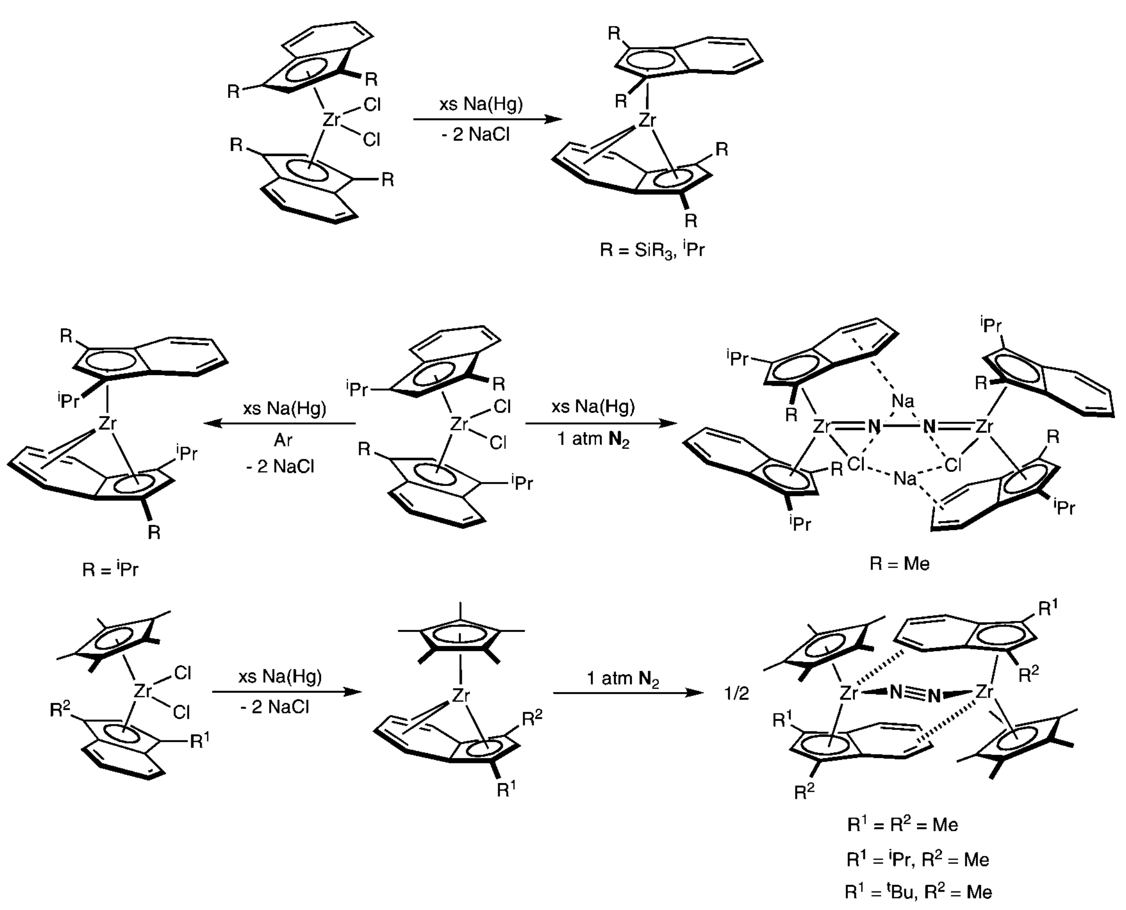


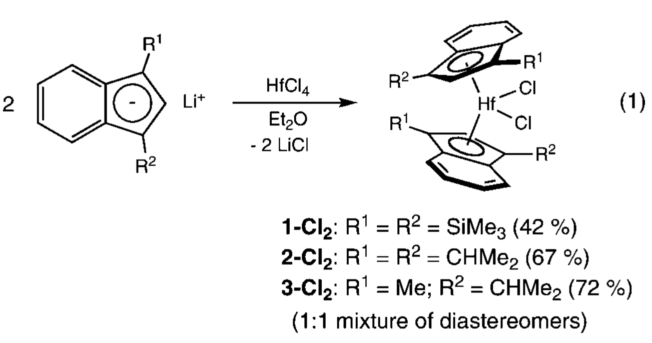
Figure 1. Synthesis and dinitrogen chemistry of bis(indenyl)zirconium complexes.

the sterically hindered complex, Cp*(η^5-C_9H_5-1,3-$(CHMe_2)_2$)Zr, adopts a sandwich structure, while the more open Cp*(η^5-C_9H_5-1-($CHMe_2$)-3-Me)Zr complex coordinates N_2 to form a weakly activated, end-on dinitrogen compound (Figure 1).[19]

Given the challenges associated with the synthesis and isolation of reduced "zirconocenes", it is not surprising that hafnium sandwich chemistry is even less developed. Alkali metal reduction of either (η^5-C_5Me_5)$_2$HfI_2[20] or (η^5-C_5Me_4H)$_2$-HfI_2[21] yielded the corresponding "end-on" and "side-on" dinitrogen complexes, respectively. The latter compound exhibits rich N_2 functionalization chemistry including dinitrogen hydrogenation,[21] carboxylation,[8] and isocyanate cycloaddition.[9] Here we describe the study of the reduction chemistry of bis(indenyl)hafnium compounds and report the synthesis and structural characterization of a hafnocene(III) monochloride as well as unusual η^6,η^5-bis(indenyl)hafnium THF and DME (DME = 1, 2-dimethoxyethane) compounds by ligand-induced haptotropic rearrangement. Evaluation of the thermal stability and additional reactivity studies establish that both the THF and DME derivatives serve as isolable sources of hafnium(II).

Results and Discussion

Synthesis and Characterization of η^6,η^5-Bis(indenyl) Hafnium THF and DME Compounds. Based on the results of our studies in bis(indenyl)zirconium chemistry,[16] the synthesis of the C_{2v} symmetric, 1,3-[$SiMe_3$]- and [$CHMe_2$]-disubstituted hafnocene dichloride complexes **1-Cl$_2$** and **2-Cl$_2$** was initially targeted. Straightforward ligand metalation was accomplished by stirring 2 equiv of the appropriate lithium indenide with $HfCl_4$ in diethyl ether at 23 °C. Subsequent filtration, extraction into pentane or toluene, and recrystallization from pentane yielded the desired hafnocene dichloride complexes, **1-Cl$_2$** and **2-Cl$_2$**, in 42% and 67% yields, respectively (eq 1).



Because of the dinitrogen coordination observed with bis(indenyl)zirconium complexes with smaller ring substituents, (η^5-C_9H_5-1-Me-3-($CHMe_2$))$_2$HfCl_2 (**3-Cl$_2$**) was also synthesized. Using a method identical to that used to prepare **1-Cl$_2$** and **2-Cl$_2$**, **3-Cl$_2$** was obtained as an equimolar mixture of *rac*- and *meso*-diasteromers in 72% yield. No attempts were made to separate the isomers.

Sodium amalgam reduction of each of the hafnocene dichloride complexes in various solvents was explored in an attempt to prepare the corresponding sandwich or dinitrogen derivatives. For all three compounds, reduction in toluene yielded a complex

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[19] Pun, D.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 6047.

[20] Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

[21] Bernskoetter, W. H.; Olmos, A. V.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 1021.

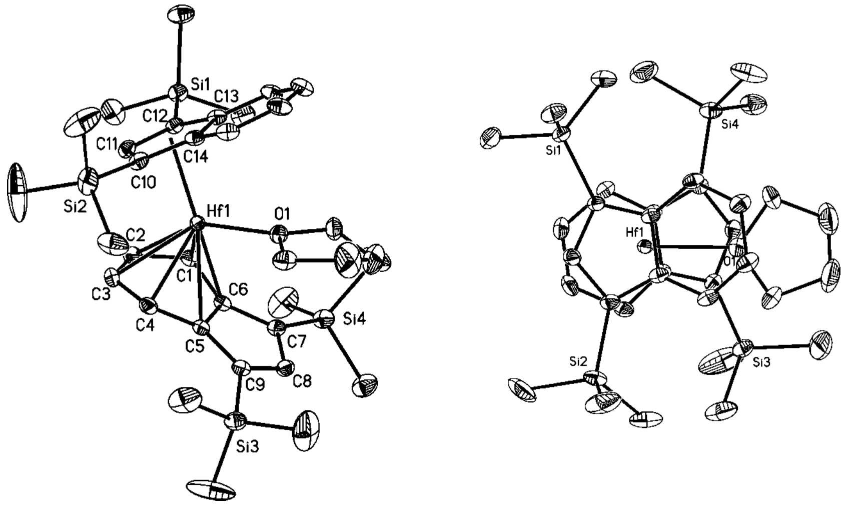
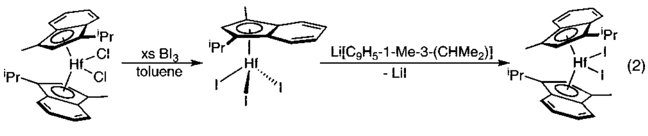


Figure 2. Solid state structure of **1-THF** with 30% probability ellipsoids and hydrogen atoms omitted for clarity. Partially labeled view (left) and top view (right).

mixture of unidentified products. These results are similar to those established in bis(cyclopentadienyl) hafnium chemistry, where sodium amalgam reduction of (η^5-C_5Me_4H)$_2$HfCl$_2$ yielded an intractable mixture of products. For the Cp compounds, this obstacle was overcome with preparation of the corresponding diiodide complex (η^5-C_5Me_4H)$_2$HfI$_2$.[21]

Inspired by these observations, the synthesis of (η^5-C_9H_5-1-Me-3-(CHMe$_2$))$_2$HfI$_2$ was pursued. Treatment of **3-Cl$_2$** with BI$_3$ in toluene did not furnish the desired diiodide complex, **3-I$_2$**, but rather the hafnocene piano stool compound (η^5-C_9H_5-1-Me-3-(CHMe$_2$))HfI$_3$ (**4-I$_3$**) was isolated as a brown powder in 63% yield (eq 2). Monitoring the reaction by ^{1}H NMR spectroscopy established that fulvene compounds, along with other unidentified organics, accompanied formation of **4-I$_3$** and account for the fate of the ejected indenyl ring. Synthesis of the desired bis(indenyl)hafnocene dichloride, **3-I$_2$**, was ultimately accomplished by treatment of **4-I$_3$** with 1 equiv of the lithium indenide Li[C_9H_5-1-Me-3-(CHMe$_2$)] in diethyl ether. Yellow **3-I$_2$** was isolated as an equimolar mixture of *rac*- and *meso*-diastereomers in 91% yield (eq 2).



(2)

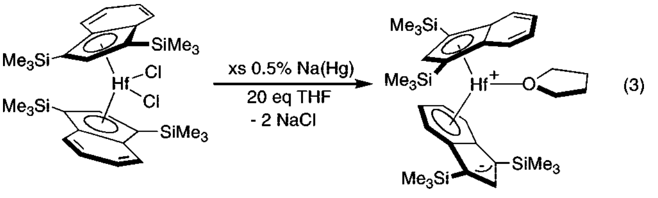
3-Cl$_2$
+ *rac* isomer

(63 %)

3-I$_2$ (91 %)
+ *rac* isomer

With the desired hafnocene diiodide in hand, reduction chemistry was explored. Stirring a toluene slurry of **3-I$_2$** with excess 0.5% sodium amalgam under vacuum or a dinitrogen atmosphere furnished a mixture of products from which variable amounts of *rac*/*meso*-(η^5-C_9H_5-1-Me-3-(CHMe$_2$))$_2$Hf(H)I (**3-(I)H**) and *rac*/*meso*-(η^5-C_9H_5-1-Me-3-(CHMe$_2$))$_2$HfH$_2$ (**3-H$_2$**) were identified. The source of the hydrogen atoms in these reductions is unknown; however observation of hydride compounds from sodium amalgam reduction of group 4 metallocene dihalides has been observed previously.[11,21] Attempts to prepare (η^5-C_9H_5-1,3-(SiMe$_3$)$_2$)$_2$HfI$_2$ (**1-I$_2$**) from analogous routes met with limited success. Importantly, no tractable η^9,η^5-bis(indenyl)hafnium sandwich compound was observed from sodium amalgam reduction using various reaction conditions.

Because the sodium amalgam reduction of **1-Cl$_2$** in toluene produced a mixture of unidentified products, focus shifted to the synthesis of the corresponding THF complex. In the case of the zirconium congener (η^6-C_9H_5-1,3-(SiMe$_3$)$_2$)(η^5-C_9H_5-1,3-(SiMe$_3$)$_2$) Zr(THF) (**5-THF**), the compound is more crystalline and is easier to isolate in pure form than the corresponding sandwich (η^9-C_9H_5-1,3-(SiMe$_3$)$_2$)(η^5-C_9H_5-1,3-(SiMe$_3$)$_2$)Zr (**5**).[22] Reduction of a diethyl ether solution of **1-Cl$_2$** with excess 0.5% sodium amalgam in the presence of 20 equiv of THF furnished a dark green solid identified as the η^6,η^5-bis(indenyl)hafnium THF compound **1-THF** (eq 3). Attempts to prepare **2-THF** from **2-Cl$_2$** using a similar protocol were unsuccessful, resulting in a mixture of unidentified products. It should be noted that the isolated zirconium sandwich (η^9-C_9H_5-1,3-(CHMe$_2$)$_2$)(η^5-C_9H_5-1,3-(CHMe$_2$)$_2$)Zr does not coordinate THF even at very high concentrations,[22] a consequence of the reluctance of electron-rich sandwiches to undergo ligand-induced haptotropic rearrangement.



(3)

1-Cl$_2$

1-THF
(70 %)

At 23 °C, the benzene-d_6 ^{1}H and ^{13}C NMR spectra of **1-THF** exhibit the number of peaks consistent with a C_s symmetric compound with inequivalent indenyl rings. Two ^{1}H NMR resonances are shifted upfield to 3.62 and 3.69 ppm and are assigned to the benzo hydrogens distal to the five-membered ring and the cyclopentadienyl hydrogen on the η^6-indenyl ring, respectively. The upfield shifting of the peaks is likely due to transannular ring currents rather than a direct consequence of the unusual hapticity. Similar effects have been observed in iridium compounds lacking η^6-indenyl coordination and in the zirconium congener **5-THF**.[22]

The solid state structure of **1-THF** was determined by X-ray diffraction (Figure 2). Two independent molecules were present in the asymmetric unit, and selected bond distances and angles for both are reported in Table 1. Also contained in Table 1 are the corresponding metrical parameters for the zirconium con-

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(22) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1-THF and 5-THF

	1-THF	1-THF	5-THF[c]
M(1)−O(1)	2.1977(16)	2.1888(15)	2.254(2)
M(1)−C(1)	2.284(2)	2.299(2)	2.340(2)
M(1)−C(2)	2.459(2)	2.462(2)	2.472(3)
M(1)−C(3)	2.455(2)	2.460(2)	2.493(2)
M(1)−C(4)	2.294(2)	2.283(2)	2.355(3)
M(1)−C(5)	2.475(2)	2.441(2)	2.468(3)
M(1)−C(6)	2.448(2)	2.469(2)	2.487(3)
M(1)−C(10)	2.470(2)	2.473(2)	2.623(3)
M(1)−C(11)	2.410(2)	2.434(2)	2.501(3)
M(1)−C(12)	2.445(2)	2.483(2)	2.454(3)
M(1)−C(13)	2.575(2)	2.600(2)	2.494(2)
M(1)−C(14)	2.602(2)	2.590(2)	2.608(3)
C(1)−C(2)	1.427(3)	1.443(3)	1.425(4)
C(1)−C(6)	1.463(3)	1.464(3)	1.458(4)
C(2)−C(3)	1.378(4)	1.385(3)	1.394(4)
C(3)−C(4)	1.433(4)	1.419(3)	1.414(4)
C(4)−C(5)	1.464(3)	1.469(3)	1.466(3)
C(5)−C(6)	1.432(3)	1.434(3)	1.444(3)
dihedral angle[a]	22.95(11)	22.44(18)	19.0(1)
rotational angle[b]	178.5(3)	170.6(1)	177.8(1)

[a] Defined as the deviation from planarity of the benzo ring, which is the angle between the planes formed by C(1)−C(2)−C(3)−C(4) and C(4)−C(5)−C(6)−C(1). [b] Defined as the angle formed between the plane defined by Hf(1), C(8), and the centroid between C(5)−C(6) and the plane defined by Hf(1), C(11), and the centroid between C(13)−C(14) in molecule 1. [c] Data for **5-THF** taken from ref 22.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\{[\textbf{1}\text{-Cl}]_2\text{Na}\}^-$

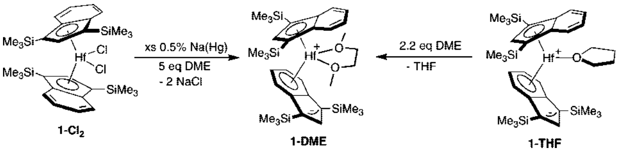
Hf(1)−Cl(1)	2.4235(9)
Hf(1)−C(1)	2.284(3)
Hf(1)−C(2)	2.479(4)
Hf(1)−C(3)	2.473(4)
Hf(1)−C(4)	2.291(3)
Hf(1)−C(5)	2.499(4)
Hf(1)−C(6)	2.478(3)
Hf(1)−C(10)	2.477(3)
Hf(1)−C(11)	2.413(3)
Hf(1)−C(12)	2.484(3)
Hf(1)−C(13)	2.612(3)
Hf(1)−C(14)	2.617(3)
C(1)−C(2)	1.408(5)
C(1)−C(6)	1.4580(5)
C(2)−C(3)	1.370(6)
C(3)−C(4)	1.437(5)
C(4)−C(5)	1.455(5)
C(5)−C(6)	1.436(5)
Na(1)−C(8)	2.722(3)
dihedral angle[a]	25.37(28)
rotational angle[b]	174.1(1)

[a] Defined as the deviation from planarity of the benzo ring, which is the angle between the planes formed by C(1)−C(2)−C(3)−C(4) and C(4)−C(5)−C(6)−C(1). [b] Defined as the angle formed between the plane defined by Hf(1), C(8), and the centroid between C(5)−C(6) and the plane defined by Hf(1), C(11), and the centroid between C(13)−C(14) in molecule 1.

gener **5-THF** for comparison. As was observed with the zirconium compound, **1-THF** adopts an idealized C_s symmetric structure where the mirror plane is perpendicular to the metallocene wedge and contains the Hf(1)−O(1) vector. The solid state structure clearly confirms the η^6,η^5 hapticity of the indenyl ligands that was established by NMR spectroscopy.

The coordinated benzo ring exhibits distortions consistent with two-electron reduction, a typical feature of zirconium compounds containing η^6-indenyl ligands.[22] For example, the six-membered rings in **1-THF** are puckered by 22.95(11)/22.44(18)° as defined by the dihedral angle formed between the planes of C(1)−C(2)−C(3)−C(4) and C(1)−C(6)−C(5)−C(4). These buckles are accompanied by relatively short Hf(1)−C(1) and Hf(1)−C(4) distances of 2.284(2)/2.299(2) and 2.294(2)/2.283(2) Å. All of the distortions to the six-membered ring in the hafnocene congener are slightly more pronounced than in the zirconium compound **5-THF**, consistent with the third-row metal being more reducing than the second.

The scope of the ligand-induced haptotropic rearrangement in reduced hafnium chemistry was further explored with 1,2-dimethoxyethane (DME). In analogous zirconium chemistry, DME proved to be an effective ligand for inducing haptotropic rearrangement and yielding a structurally characterized η^6,η^5-bis(indenyl)zirconium DME complex.[22,23] The synthesis of **1-DME** was initially accomplished by reduction of a diethyl ether solution of **1-Cl₂** with excess sodium amalgam in the presence of 5 equiv of DME. Extraction followed by recrystallization from pentane yielded a green solid identified as $[(\eta^6\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)(\eta^5\text{-C}_9\text{H}_5\text{-1,3,-(SiMe}_3)_2)\text{Hf-(C}_4\text{H}_{10}\text{O)}]$ (**1-DME**) (eq 4). Additional experimentation established that **1-DME** was more reliably synthesized by addition of an excess, typically 2.2 equiv, of 1,2-dimethoxyethane to a benzene solution of **1-THF** (eq 4).



(4)

The benzene-d_6 ^{1}H and ^{13}C NMR spectra of **1-DME** at 23 °C exhibit the number of peaks consistent with inequivalent indenyl rings and overall C_s molecular symmetry. As with **1-THF** and the zirconium examples,[22] an upfield-shifted benzo resonance was located at 3.91 ppm, consistent with η^6,η^5 indenyl hapticity.

During attempts to recrystallize **1-DME** faint yellow crystals were isolated. Single-crystal X-ray diffraction established the molecular structure not as the expected **1-DME** compound but as an unusual sodium chloride compound, $\{[\textbf{1}\text{-Cl}]_2\text{Na}\}\{\text{Na(DME)}_3\}$. The ^{1}H NMR spectrum of the single crystals established a diamagnetic compound with idealized C_s symmetry and inequivalent indenyl rings. A diagnostic upfield-shifted benzo resonance was observed at 3.64 ppm, diagnostic of η^6-hapticity. The sodium-coordinated DME was confirmed with the observation of broad resonances centered at 1.27 (Me) and 1.61 (CH₂) ppm, likely due to rapid and reversible dissociation−coordination in benzene-d_6 solution.

The solid state structure of the anion is presented in Figure 3 and establishes the identity of the molecule. The cation, Na(DME)₃, was severely disordered, and the SQUEEZE program was used to remove it from the final solution of the anion. This approach includes only the sodium cation and dramatically improved the *R*-factor of the final solution. For the anion, a dimeric structure is observed with a bridging sodium atom that is bound to the hafnium chlorides ($d_{\text{Na-Cl}} = 2.5860(10)$ Å) and the unsubstituted cyclopentadienyl carbon ($d_{\text{Na-C}} = 2.722(3)$ Å) of the η^6-coordinated indenyl ligand. The geometry of the sodium atom is best described as idealized square planar with the sum of the angles being 360.00(16)°.

As is typical for zirconium and hafnium complexes with η^6,η^5-indenyl ligands, the rings are *anti* with a rotational angle of 174.1(1)°, likely to minimize transannular interactions between the bulky indenyl substituents. The distortions in the

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(23) Bradley, C. A.; Veiros, L. F.; Chirik, P. J. *Organometallics* **2007**, *26*, 3191.

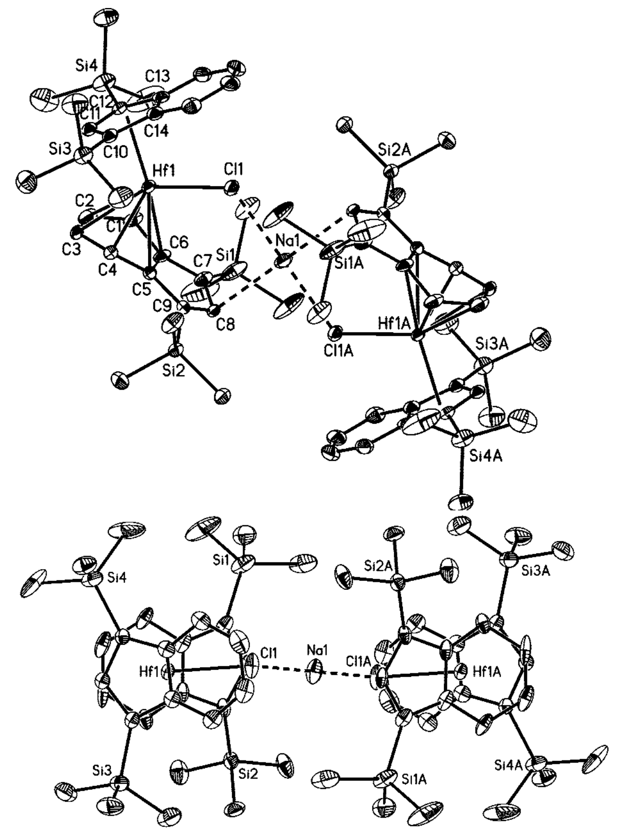
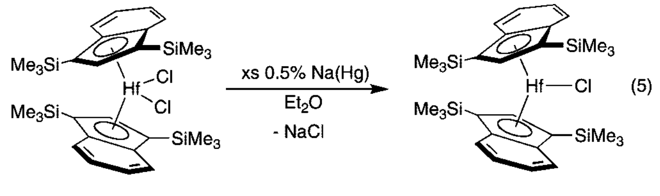


Figure 3. Solid state structure of the anion **{[1-Cl]$_2$Na}**$^-$ with 30% probability ellipsoids and hydrogen atoms omitted for clarity.

bound benzo ring are consistent with two-electron reduction with a relatively large dihedral angle of 25.37(28)°, comparable to **1-THF**.

Interestingly, treatment of benzene-d_6 solutions of **{[1-Cl]$_2$Na}{Na(DME)$_3$}** (these solutions also contain variable amounts of **1-DME**) with 1 atm of CO resulted in precipitation of sodium chloride and formation of the hafnocene dicarbonyl complex **1-(CO)$_2$**. No **1-Cl$_2$** was detected by ^{1}H NMR spectroscopy, suggesting that **{[1-Cl]$_2$Na}{Na(DME)$_3$}** behaves more like a sodium chloride complex of Hf(II) rather than a Hf(III) monochloride compound (*vide infra*).

Additional solvents were screened for the sodium amalgam reduction of **1-Cl$_2$**. More hindered THF ligands were of particular interest, as it was hoped that less donating cyclic ethers would stabilize reactive intermediates and prevent decomposition but not bind as strongly as the THF and DME ligands in **1-THF** and **1-DME**, respectively. Reduction of a diethyl ether solution of **1-Cl$_2$** with excess 0.5% sodium amalgam in the presence of excess 2,5-dimethyl or 2-methyl THF resulted in isolation of a green solid identified as the bis(indenyl)hafnocene chloride complex **1-Cl** (eq 5). Performing the reduction reaction in pure diethyl ether also produced the same product and proved a more reproducible and convenient protocol.



1-Cl$_2$ **1-Cl**

The molecular structure of **1-Cl** was determined by single-crystal X-ray diffraction and is presented in Figure 4. Two independent molecules were located in the asymmetric unit, and data from both compounds are presented in Table 3. Both rings are η^5-coordinated and exhibit metrical parameters consistent with typical bent metallocenes of hafnium. The two indenyl rings are nearly eclipsed with rotational angles of 31.8(1)° and 27.2(1)°. The [SiMe$_3$] substituents are geared in a manner to avoid transannular interactions. As expected for a bent metallocene, the chloride ligand is located in the center of the metallocene wedge with Hf−Cl bond distances of 2.3807(7) and 2.3855(8) Å.

The structural data establish a rare example of a crystallographically characterized, monomeric hafnium(III) complex. Several bis(cyclopentadienyl)zirconium(III) monohalide compounds have been synthesized and structurally characterized. Depending on the specific cyclopentadienyl substitution pattern, these compounds can be either diamagnetic or paramagnetic. For example, $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2$[24] and $[(\eta^5\text{-}C_5H_4\text{-}SiMe_3)_2ZrX]_2$ (X = Cl, I)[25] are both dimeric and diamagnetic, owing to antiferromagnetic coupling between the two Zr(III) centers.[26] More substituted zirconocenes such as $[(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2)_2\text{-}ZrCl]_2$ are dimeric but have weak interactions between the metal centers and are hence paramagnetic.[25] In one case, a monomeric, paramagnetic compound, $(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}{}^tBu)_2ZrCl$, was structurally characterized.[27]

By comparison, there is a paucity of well-defined, structurally authenticated hafnium(III) compounds. Reduction of HfI_4 with metallic aluminum was reported to yield HfI_3.[28] Cotton[29] and Girolami[30,31] have obtained the solid state structures of diamagnetic, dimeric hafnium(III) phosphine compounds purported to have metal−metal bonds. In metallocene chemistry, bis(cyclopentadienyl)hafnium(III) monohalide compounds are rare[27] and, to our knowledge, lack structural characterization. Reduction of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ with sodium amalgam reportedly yields $[(\eta^5\text{-}C_5H_5)_2HfCl]_2$, which was formulated as a dimer based on limited spectroscopic and other analytical data.[32]The hafnium(III) anion of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ was generated electrochemically[33] and observed by EPR spectroscopy (g_{av} = 1.9839). Lappert has reported the EPR spectrum (g_{av} = 1.9887) of the hafnium(III) alkyl $(\eta^5\text{-}C_5H_4\text{-}{}^iPr)_2HfCH_2SiMe_3$,[34] as well as a hafnocene dialkyl anion (g_{av} = 1.987).[35]

In addition to X-ray diffraction, **1-Cl** was also characterized by solution spectroscopic techniques. The benzene-d_6 ^{1}H NMR spectrum of **1-Cl** at 23 °C exhibits a single broad ($\Delta\nu_{1/2}$ = 287 Hz) resonance centered at 5.72 ppm likely due to the [SiMe$_3$] substituents. Toluene solution and glass EPR measurements were

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(24) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; De Boer, J. L. *Organometallics* **1989**, *8*, 250.

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

(26) (a) DeKock, R. L.; Peterson, M. A.; Reynolds, L. E. L.; Chen, L.-H.; Baerends, E. J.; Vernooijs, P. *Organometallics* **1993**, *12*, 2794. (b) Bénard, M.; Rohmer, M.-M. *J. Am. Chem. Soc.* **1992**, *114*, 4785.

(27) Urazowski, I. F.; Ponomaryev, V. I.; Nifant'ev, I. E.; Lemenovskii, D. A. *J. Organomet. Chem.* **1989**, *368*, 287.

(28) Baker, W. A.; Janus, A. R. *J. Inorg. Nucl. Chem.* **1964**, *26*, 2087.

(29) Cotton, F. A.; Kibla, P. A.; Wojtczak, W. A. *Inorg. Chim. Acta* **1990**, *177*, 1.

(30) Morse, P. M.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 3200.

(31) Riehl, M. E.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1993**, *32*, 218.

(32) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *293*, 61.

(33) Fakhr, A.; Mugnier, Y.; Gautheron, B.; Laviron, E. *J. Organomet. Chem.* **1986**, *302*, C7.

(34) Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc. Dalton* **1981**, 805.

(35) Lappert, M. F.; Raston, C. L. *Chem. Commun.* **1980**, 1284.

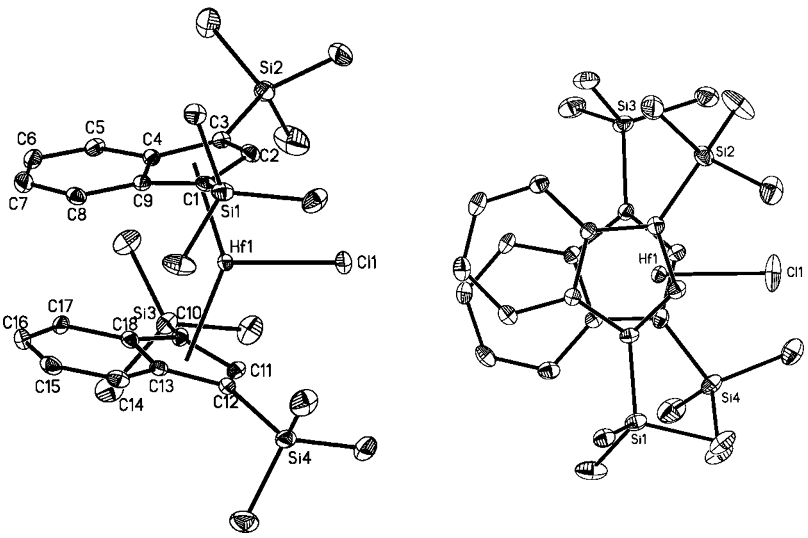

Figure 4. Solid state structure of **1-Cl** with 30% probability ellipsoids. Only one of the independent molecules found in the asymmetric unit is shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Two Independent Molecules of 1-Cl in the Asymmetric Unit

	1-Cl		1-Cl
Hf(1)−Cl(1)	2.3807(7)	Hf(2)−Cl(2)	2.3855(8)
Hf(1)−C(1)	2.451(2)	Hf(2)−C(31)	2.436(3)
Hf(1)−C(2)	2.417(2)	Hf(2)−C(32)	2.433(3)
Hf(1)−C(3)	2.481(3)	Hf(2)−C(33)	2.489(3)
Hf(1)−C(4)	2.580(3)	Hf(2)−C(34)	2.556(3)
Hf(1)−C(9)	2.574(2)	Hf(2)−C(39)	2.539(3)
Hf(1)−C(10)	2.436(2)	Hf(2)−C(40)	2.447(3)
Hf(1)−C(11)	2.438(2)	Hf(2)−C(41)	2.423(3)
Hf(1)−C(12)	2.492(3)	Hf(2)−C(42)	2.481(3)
Hf(1)−C(13)	2.556(2)	Hf(2)−C(43)	2.592(3)
Hf(1)−C(18)	2.543(2)	Hf(2)−C(48)	2.592(3)
C(5)−C(6)	1.359(4)	C(35)−C(36)	1.350(4)
C(6)−C(7)	1.401(4)	C(36)−C(37)	1.420(4)
C(7)−C(8)	1.360(4)	C(37)−C(38)	1.353(4)
C(14)−C(15)	1.368(4)	C(44)−C(45)	1.353(4)
C(15)−C(16)	1.400(4)	C(45)−C(46)	1.404(4)
C(16)−C(17)	1.367(4)	C(46)−C(47)	1.350(4)
indenyl fold angles[a]	8.79(9)/8.21(15)	indenyl fold angles	7.96(16)/9.63(8)
dihedral angle[b]	2.63(13)/2.59(28)	dihedral angles	3.02(25)/2.64(19)
rotational angle[c]	31.8(1)	rotational angle	27.2(1)

[a] Defined as the angle between the planes formed by the five-membered cyclopentadienyl and the six-membered benzo rings of the indenyl. [b] Defined as the deviation from planarity of the benzo ring, which is the angle between the planes formed by C(5)−C(4)−C(9)−C(8) and C(5)−C(6)−C(7)−C(8) in molecule 1. [c] Defined as the angle formed between the plane defined by Hf(1), C(2), and the centroid between C(4)−C(9) and the plane defined by Hf(1), C(11), and the centroid between C(13)−C(18) in molecule 1.

made over a range of temperatures, and a representative spectrum collected at 77 K is presented in Figure 5. Spectra recorded at 5, 26, 50, and 293 K are reported in the Supporting Information. At 77 K, a rhombic signal is observed for **1-Cl** with $g_x = 1.98$, $g_y = 1.96$, and $g_z = 1.70$. Hyperfine coupling to both spin-active hafnium nuclei, ^{179}Hf ($S = 9/2$) and ^{177}Hf ($S = 7/2$), is observed.

A preliminary survey of the reactivity of **1-Cl** was conducted. Addition of 1 atm of carbon monoxide to a benzene-d_6 solution of **1-Cl** induced disproportionation and yielded a near equimolar mixture of the hafnocene dichloride **1-Cl$_2$** and the dicarbonyl **1-(CO)$_2$**. This reaction is typical of zirconocene(III) monohalide compounds.[24,25] In one-electron chemistry, **1-Cl** is an efficient chlorine atom acceptor, as addition of $PbCl_2$ cleanly furnished the hafnocene dichloride compound **1-Cl$_2$**.

Reactivity of 1-THF and 1-DME. The reactivity of the η^6,η^5-bis(indenyl)hafnium ligand complexes was examined to determine whether **1-THF** and **1-DME** could serve as convenient and isolable sources of divalent bis(indenyl)hafnium. The lability of the coordinated THF was evaluated with an isotopic labeling experiment. Addition of excess THF-d_8 to a benzene-d_6 solution of **1-THF** yielded a mixture of **1-THF** and **1-THF-d_8** over the course of minutes at 23 °C. The isolation of **1-DME** and previous kinetic studies with the zirconium congener **5-THF**[22] suggest that THF exchange is likely associative.

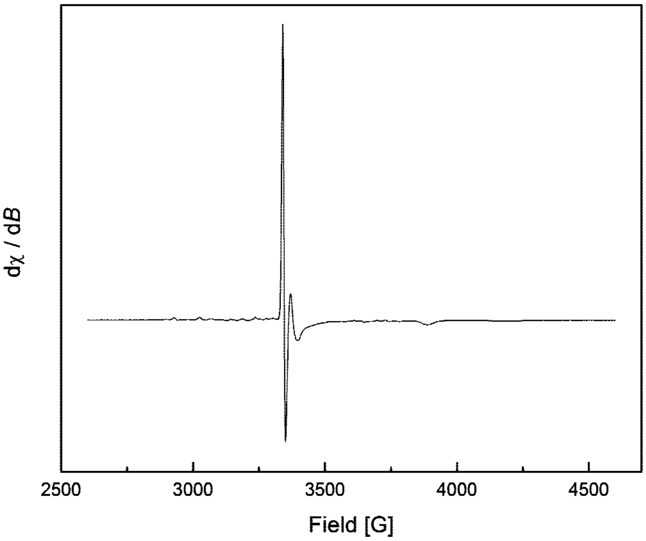

Figure 5. Toluene glass EPR spectrum of **1-Cl** recorded at 77 K.

The thermal stability of **1-THF** was also evaluated. Thermolysis of the zirconium compound **5-THF** at 85 °C resulted in C−O bond cleavage and yielded the ring-opened zirconium(IV) product $(\eta^5\text{-}C_9H_5\text{-}1,3\text{-}(SiMe_3)_2)_2Zr(\mathit{cyclo}\text{-}O(CH_2)_3CH_2)$.[36,37] For the hafnocene complex, warming a benzene-d_6 solution of **1-THF** to 85 °C produced a mixture of products, depending on the concentra-

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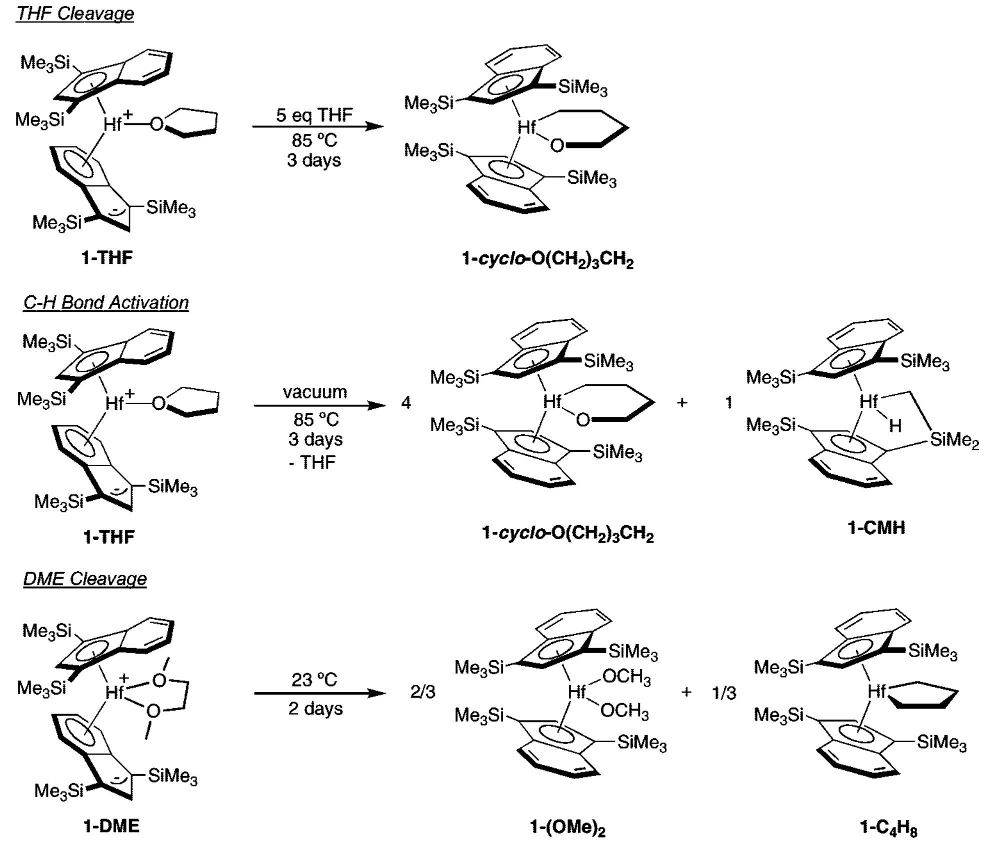
(36) Bradley, C. A.; Veiros, L. F.; Pun, D.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 16600.

(37) For related C−O bond cleavage chemistry with reduced group 4 metallocenes see: (a) Beweries, T.; Burlakov, V. V.; Bach, M. A.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 247. (b) Beweries, T.; Jäger-Fiedler, U.; Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 3000.

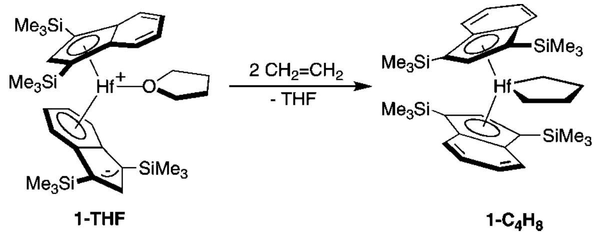
Scheme 1



tion of THF. When the thermolysis was conducted in the presence of 5 equiv of THF, the predominant product was that arising from C−O bond cleavage, (η^5-C_9H_5-1,3-$(SiMe_3)_2)_2$Hf-(*cyclo*-$O(CH_2)_3CH_2$) (**1-*cyclo*-$O(CH_2)_3CH_2$**) Scheme 1).

In contrast, allowing a benzene-d_6 solution of **1-THF** to stand at ambient temperature under vacuum produced a 2.7:1 mixture of **1-*cyclo*-$O(CH_2)_3CH_2$** and a new C_1 symmetric compound, identified as the hafnium cyclometalated hydride **1-CMH** (Scheme 1). Repeating the reaction at 85 °C resulted in a 4:1 mixture of **1-*cyclo*-$O(CH_2)_3CH_2$** to **1-CMH**. The observation of **1-CMH** following THF loss suggests that C−H oxidative addition to the putative η^5,η^5-bis(indenyl)hafnium is facile, more facile than the benzo ring coordination; thus the desired η^9,η^5-bis(indenyl)hafnium sandwich complex was not observed.

For **1-DME**, C−O bond cleavage was more rapid. Allowing a benzene-d_6 solution of the compound to stand at 23 °C resulted in smooth conversion to the bis(indenyl)hafnocene bis(methoxide) **1-$(OMe)_2$** and metallocyclopentane **1-C_4H_8** in an approximate 2:1 ratio (Scheme 1). The latter derives from the reductive coupling of 2 equiv of ethylene, unlike the zirconium congener, where the ethylene complex was isolated from DME cleavage. **1-C_4H_8** was independently synthesized by addition of ethylene to **1-THF** (eq 6). Attempts to isolate the bis(indenyl)hafnocene ethylene compound by addition of substoichiometric amounts of olefin resulted in partial conversion to **1-C_4H_8**.



(6)

Comparison of the Electronic Structures of Bis(indenyl)-zirconium and Hafnium Complexes. Bis(indenyl)hafnium dicarbonyl compounds were synthesized to evaluate the electronics of the metal center as compared to the zirconium congeners.[18,38] Exposure of a pentane solution of **1-THF** to 4 atm of carbon monoxide for two days at 23 °C followed by solvent removal and recrystallization from pentane at −35 °C furnished a dark solid identified as **1-$(CO)_2$** (Figure 6). Because THF and DME complexes of the alkylated bis(indenyl)hafnium compounds were not isolated, the corresponding hafnocene dicarbonyl complexes were prepared by alkali metal reduction of the dichloride compounds under a CO atmosphere.

With a family of dicarbonyl complexes in hand, the infrared spectrum of each complex in pentane was recorded. The silylated hafnocene dicarbonyl **1-$(CO)_2$** exhibits *six* CO bands, similar to the zirconium congener. Two bands are expected for a bent metallocene dicarbonyl. The additional bands were attributed to the presence of different rotamers that have different carbonyl stretching frequencies. It is remarkable that the relative orientation of the indenyl rings has such a measurable impact on the carbonyl stretching frequencies. The zirconocene and hafnocene dicarbonyl complexes with smaller indenyl substituents exhibit fewer carbonyl bands due to either population of fewer rotamers or the rotamers having indistinguishable CO stretching frequencies.

The general trend established for bis(indenyl)zirconium dicarbonyl compounds also holds for the corresponding hafnium compounds. The silylated hafnocene **1-$(CO)_2$** is the least electron rich in the series, while introduction of alkyl substituents on the indenyl ring produces more reducing hafnium centers (Figure

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(38) Bradley, C. A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H. D.; Chirik, P. J. *Organometallics* **2004**, *23*, 5332.

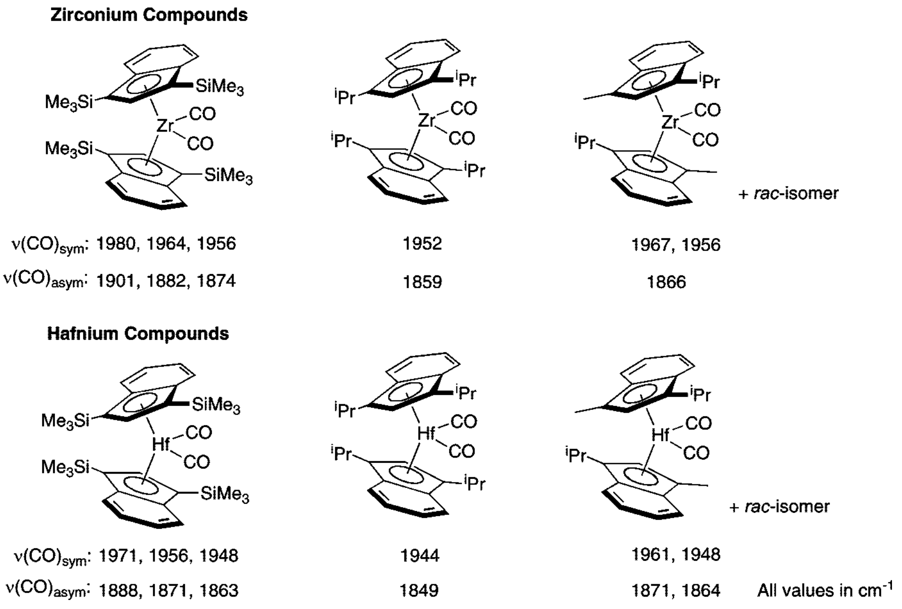


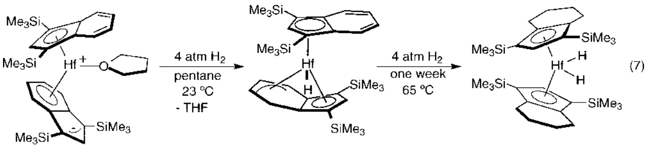
Figure 6. Carbonyl stretching frequencies for bis(indenyl)zirconium and hafnium complexes.

6). Comparison of zirconium and hafnium congeners establishes that the third-row metal, as expected, is more reducing.

Oxidative Addition Chemistry: H_2 Addition and C−H Bond Activation Studies. Bis(indenyl)zirconium and hafnium hydride complexes are of interest due to their potential application as initiators in olefin polymerization catalysis[39] as well as in catalytic bond-forming reactions used in small-molecule catalysis such as olefin and imine hydrogenation.[40] The putative monomeric hafnocene dihydride, **1-H$_2$**, could in principle undergo H_2 reductive elimination and provide a mild synthetic route to the desired η^9,η^5-bis(indenyl)hafnium sandwich. Fundamental studies of oxidative addition reactions at a reduced hafnium center are also rare owing to the paucity of isolable Hf(II) complexes. For these reasons, the oxidative addition of H_2 and C−H bonds to **1-THF** was studied.

Exposure of a pentane solution of **1-THF** to 4 atm of dihydrogen resulted in a rapid color change from dark green to yellow. Analysis of the isolated tan solid by ^1H and ^{13}C NMR spectroscopy established formation of a C_1 symmetric hafnocene product. The benzene-d_6 ^1H NMR spectrum exhibits a hafnium hydride peak centered at 3.03 ppm and methylene multiplets centered at 2.32 and 2.51 ppm. These spectral features are consistent with formation of (η^5-C_9H_5-1,3($SiMe_3)_2$)(η^5,η^3- C_9H_6-1,3($SiMe_3)_2$)HfH (**1-DHID-H**), where a hydrogen has migrated to one of the indenyl rings to form an unusual η^5,η^3-4,5-dihydroindenediyl (DHID) ligand (eq 7).

There are two possible diastereomers of **1-DHID-H**, defined by the relative orientation of the hafnium hydride and the newly formed methylene carbon. The case where these two groups are in proximity has been designated *syn*, where they are opposite, *anti*. In zirconium chemistry, both diastereomers were isolated and crystallographically characterized.[42] The *syn* isomer was obtained from hydrogen addition to the sandwich, while the *anti* was observed from treatment of the THF complex with H_2. Over time, the *anti* zirconium DHID complex isomerized to the *syn* isomer. In hafnocene chemistry, the hydrogenation of **1-THF** yielded only the *syn* diastereomer, the stereochemistry of which was established by NOESY NMR spectroscopy (Figure 7).



1-THF syn-1-DHID-H 1-THI-H$_2$ (7)

The protons of the six-membered ring of the dihydroindenediyl ligand were the first resonances assigned on the basis of both NOE correlations and chemical shifts. Using this approach, the resonances at 2.32 and 2.51 ppm were assigned as the methylene protons. Cross-peaks between the hafnium hydride and the latter methylene proton (the *endo* position) and the proton on the adjacent allylic carbon indicate that this compound is in the *syn* conformation. The absence of correlations between the hafnium hydride and other allylic protons further corroborates this assignment.

A deuterium labeling study was also conducted to provide additional support for the NMR assignments and the observed reaction chemistry. Exposure of a benzene-d_6 solution of **1-THF** to 4 atm of D_2 gas yielded **1-DHID-*d$_1$*-D** and established exclusive deuterium incorporation into the hafnium-hydride (deuteride) and the *endo* methylene position on the dihydroindenediyl ring (eq 8).

As in the zirconium chemistry,[42] **1-DHID-H** is an intermediate during benzo ring hydrogenation and formation of the corresponding tetrahydroindenyl compound, **1-THI-H$_2$**. However, complete conversion of **1-DHID-H** to **1-THI-H$_2$** required heating at 65 °C for one week under 4 atm of dihydrogen. The final product was characterized by the appearance of ^1H NMR resonances in the vicinity of 2 ppm and the appearance of a

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(39) (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Brintzinger, H. H.; Fisher, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143.

(40) (a) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562. (b) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. (c) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703. (d) Troutman, M. V.; Apella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4916.

(41) Chirik, P. J.; Bercaw, J. E. *Organometallics* **2005**, *24*, 5407.

(42) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 6454.

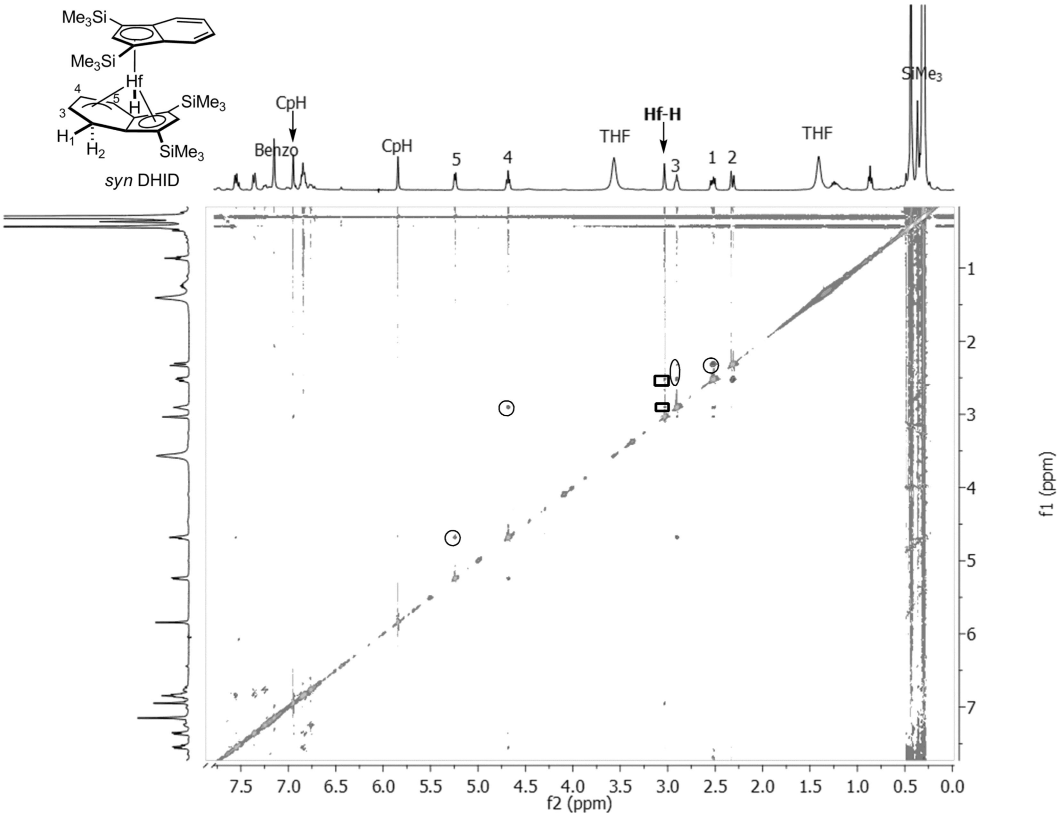
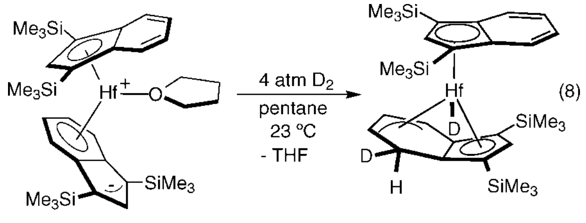
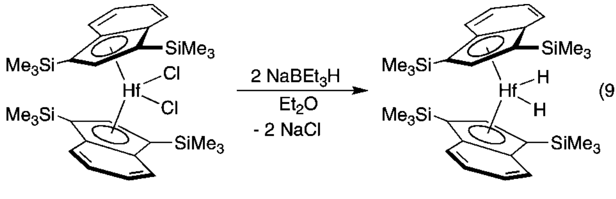


Figure 7. NOESY NMR spectrum of ***syn*-1-DHID-H**. Circles and ovals depict assignment of the dihydroindenediyl ring, while bold squares the orientation of the Hf-*H* over H_1 and H_3.



1-THF **1-DHID-d_1-D**

(8)



1-Cl$_2$ **1-H$_2$**

(9)

hafnium hydride at 14.95 ppm, consistent with a monomer in benzene-d_6.[20,41]

Hydrogenation of the corresponding zirconium compound, **5-THF**, also yielded a zirconium hydride complex with an η^5,η^3-4,5-dihydroindenediyl (DHID) ligand.[42] As in the hafnium case, no intermediate zirconocene dihydride (or THF adduct) was observed by ^{1}H NMR spectroscopy. For a family of zirconium dihydride complexes, THF was shown to accelerate the rate of rearrangement.

Because dihydrogen addition to **1-THF** did not yield an observable hafnocene dihydride prior to rearrangement to **1-DHID-H**, alternative routes for the synthesis of **1-H$_2$** were explored. Treatment of **1-Cl$_2$** with 2 equiv of a toluene solution of $NaBEt_3H$ followed by filtration and recrystallization from pentane furnished the desired hafnocene dihydride complex, **1-H$_2$** (eq 9). The benzene-d_6 ^{1}H NMR spectrum of white **1-H$_2$** exhibits the number of peaks consistent with a C_{2v} symmetric hafnocene. The hafnium hydride peak appears downfield at 14.85 ppm, consistent with a monomer in solution.[41]

Upon addition of excess H_2, the hafnium hydride resonance of **1-H$_2$** broadens, a result of fast exchange between free dihydrogen and the Hf-H positions. Addition of 4 atm of D_2 to a benzene-d_6 solution of **1-H$_2$** at 23 °C immediately formed **1-D$_2$** upon mixing.

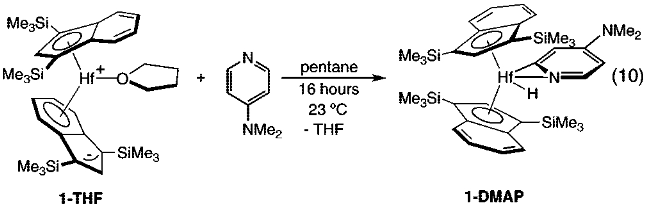
Isolation of **1-H$_2$** allowed evaluation of its potential intermediacy in the isomerization to **1-DHID-H**. Allowing a benzene-d_6 solution of **1-H$_2$** to stand at 23 °C resulted in only trace amount of the isomerization product after several days. Heating the sample to 65 °C did not induce additional conversion. Because these results demonstrate that THF likely plays a role in formation of **1-DHID-H**, various amounts of THF were added to a benzene-d_6 solution of **1-H$_2$**. The results of these studies are summarized in Table 4.

Increased amounts of THF favor the isomerization of **1-H$_2$** to **1-DHID-H**. Because the reactions occurred immediately after mixing and do not change over the course of days at 23 °C, the conversions in Table 4 represent equilibria. Interestingly, complete conversion of **1-H$_2$** to **1-DHID-H** was never observed in contrast to the hydrogenation of **1-THF** (with only 1 equiv of THF), where no **1-H$_2$** was detected by ^{1}H NMR spectroscopy. These studies establish that the hydrogenation of **1-THF** does not produce **1-H$_2$** as an intermediate on the isomerization pathway and that H_2 oxidative addition likely occurs directly at the η^6 compound. Similar results were obtained with deuterium labeling as addition of excess THF to a benzene-d_6 solution of **1-D$_2$** resulted in exclusive isotopic incorporation into the hafnium-hydride (deuteride) position along with the *endo* methylene in the dihydroindenediyl ring of **1-DHID-D**.

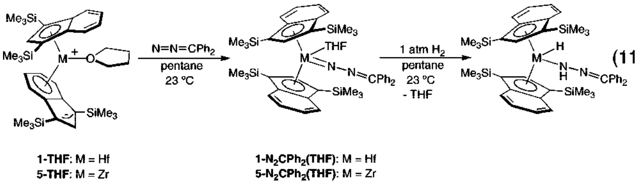
Table 4. Conversion of 1-H_2 to 1-DHID-H as a Function of Added THF

equiv of added THF	% conversion
1	66
10	84
50	94

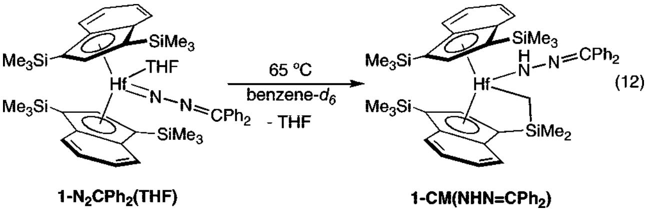
The oxidative addition of aromatic C−H bonds was also explored. For reduced complexes of both bis(indenyl)[43] and bis(cyclopentadienyl)zirconium,[44] *N*,*N*-dimethylaminopyridine (DMAP) has proven to be a useful substrate, participating in facile C−H bond activation under relatively mild conditions. Stirring a pentane solution of **1-THF** with 1 equiv of DMAP for 16 h at 23 °C resulted in clean C−H activation chemistry to yield the *ortho*-metalated product, **1-DMAP**, as a fluffy white powder (eq 10). The ^{1}H and ^{13}C NMR spectra recorded in benzene-d_6 exhibit the number of peaks consistent with C_s symmetry. One notable feature is the observation of the hafnium hydride centered at 6.93 ppm.



Reactions with N_2CPh_2. With potential divalent hafnocene sources in hand, the synthesis of hafnium alkylidene complexes by N_2 displacement from diazoalkanes was explored. Hafnium alkylidenes are known,[45,46] but the lone isolable example was prepared by α-hydrogen abstraction of a dialkyl derivative. Treatment of **1-THF** with N_2CPh_2 in pentane solution furnished an orange, C_s symmetric compound identified as the hafnocene diazoalkane complex with a molecule of coordinated THF, **1-N_2CPh_2(THF)** (eq 11).

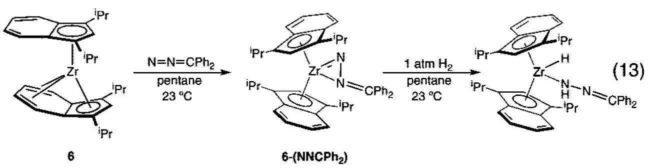


The reactivity of **1-N_2CPh_2(THF)** was briefly explored. Previously our laboratory reported the 1,2-addition of dihydrogen to the bis(cyclopentadienyl) titanium diazoalkane complex (η^5-C_5H_3-1,3-$(SiMe_3)_2)_2Ti(N_2CPh_2)$.[14] Addition of 1 atm of dihydrogen to a benzene-d_6 solution to **1-N_2CPh_2(THF)** for 2 h at 23 °C produced an orange solid identified as the product of H_2 1,2-addition, **1-NHNCPh$_2$(H)**, with loss of free THF (eq 11). Notable ^{1}H NMR spectroscopic features include observation of an N−H peak centered at 6.22 ppm and the hafnium hydride at 9.31 ppm. Attempts to induce N_2 loss by heating the sample to 65 °C for 24 h resulted in 1,2-addition of a $SiMe_3$ C−H across the hafnium imido bond to form **1-CM(NHN=CPh$_2$)** (eq 12). Only one diasteromer was observed by NMR spectroscopy but was not assigned.



Based on these results, similar chemistry was explored with the zirconium congener, **5-THF**. Addition of N_2CPh_2 to **5-THF** also furnished the zirconocene diazoalkane complex with a molecule of coordinated THF. Similar to its hafnocene congener, **5-N_2CPh_2(THF)** undergoes rapid hydrogenation to form Zr−H and N−H bonds via 1,2-addition (eq 11).

Because N_2 loss from the diazoalkane derivatives of the silylated metallocenes was not observed, similar chemistry with a smaller, more electron-rich bis(indenyl)zirconium sandwich was explored. Addition of N_2CPh_2 to a pentane solution of the base-free zirconocene sandwich, **6**, furnished a C_s symmetric product identified as the zirconocene η^2-diazoalkane complex (eq 13). Attempts to induce N_2 loss by thermolysis were unsuccessful. Warming a benzene-d_6 solution of the compound to 65 °C for two days produced no change; additional heating to 95 °C resulted in decomposition by fulvene loss. As with the silyl-substituted metallocene diazoalkane complexes, **6-N_2CPh_2** undergoes rapid hydrogenation (eq 13). Diagnostic N−H and Zr−H resonances were observed by ^{1}H NMR spectroscopy.



Concluding Remarks

The chemistry of reduced bis(indenyl)hafnium compounds has been explored. While the η^9,η^5-bis(indenyl)hafnium sandwich has thus far eluded isolation, ligand-induced haptotropic rearrangements with THF and DME have proven to be a successful strategy for the synthesis of η^6,η^5-bis(indenyl)hafnium ligand compounds. Changing the medium of the reduction reaction to diethyl ether resulted in isolation and crystallographic characterization of a rare bis(indenyl)hafnium(III) complex. Crystallographic characterization of the THF derivative as well as infrared spectroscopy on dicarbonyl complexes establishes that the hafnium is more reducing than zirconium in analogous compounds.

The increased reduction potential of the hafnocene congeners manifests in the reactivity of the compounds. In the absence of excess THF, the η^6,η^5-bis(indenyl)hafnium THF compound undergoes competitive cyclometalation of an indenyl [$SiMe_3$] substituent along with C−O bond cleavage. The observation of facile C−H activation demonstrates that if formed, the η^5,η^5-bis(indenyl)hafnium undergoes oxidative addition rather than benzo ring coordination.

Other observed reactivity demonstrates the utility of the THF complex as an isolable hafnium(II) source. Facile oxidative addition of dihydrogen and an aromatic C−H bond of *N*,*N*-dimethylaminopyridine were observed. In the former case, the presence of THF facilitated isomerization to a dihydroindenyl

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

(44) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 1092.

(45) Fryzuk, M. D.; Duval, P. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1608.

(46) For examples of hafnium alkylidenes prepared by laser ablation: (a) Cho, H. G.; Andrews, L. *Organometallics* **2004**, *23*, 4357. (b) Cho, H. G.; Wang, X. F.; Andrews, L. *Organometallics* **2005**, *24*, 2854.

hafnium hydride derivative, which is an intermediate to the corresponding tetrahydroindenyl hafnium dihydride. Reactivity studies with diphenyldiazomethane were also conducted, and hydrogenation of the coordinated diazoalkane by 1,2-addition was observed.

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.[47] Benzene-d_6 and toluene-d_8 for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves or sodium metal. Dichloromethane-d_2 was distilled from CaH_2 under vacuum prior to use. Chlorotrimethylsilane was purchased from Acros Organics and dried over CaH_2 before use. Carbon monoxide was purchased from Aldrich and was passed through a liquid nitrogen cooled trap before use. Both C_9H_6-1,3-$(SiMe_3)_2$[48,49] and Li[C_9H_5-1,3-$(SiMe_3)_2$][49] were prepared according to literature procedures.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.779 MHz (^{1}H) and 110.524 MHz (^{13}C), respectively. Two-dimensional NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 500.62 Hz. All chemical shifts are reported relative to $SiMe_4$ using ^{1}H (residual) or ^{13}C NMR chemical shifts of the solvent as a secondary standard. Infrared spectroscopy was conducted on a Thermo Nicolet spectrometer. X-Band ESR spectra were recorded on a Bruker EMX spectrometer at a frequency of 9.55 GHz under standard conditions in 4 mm i.d. quartz tubes. The tubes were sealed under vacuum at 77 K. Spectra at temperatures 4.2−77 K were recorded using a liquid helium cryostat, ESR-10 (Oxford Instruments Ltd., England).

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

Preparation of (η^5-C_9H_5-1,3$(SiMe_3)_2)_2HfCl_2$ (1-Cl_2). A 500 mL round-bottomed flask was charged with 3.65 g (13.7 mmol) of Li[C_9H_5-1,3$(SiMe_3)_2$] and approximately 150 mL of diethyl ether. The resulting yellow solution was chilled in a cold well cooled to liquid nitrogen temperature, and 2.19 g (6.85 mmol) of $HfCl_4$ was added. The reaction mixture was stirred for one day, and the solvent was removed *in vacuo*. The resulting solid was dissolved in dichloromethane and filtered through a pad of Celite. Removal of dichloromethane *in vacuo* yielded a brown oil that was recrystallized from diethyl ether at −35 °C to afford 2.21 g (42%) of **1-Cl_2** as a yellow solid. Anal. Calcd for $C_{30}H_{46}Si_4HfCl_2$: C, 46.89; H, 6.03. Found: C, 46.75; H, 6.23. ^{1}H NMR (benzene-d_6): δ 0.37 (s, 36H, $SiMe_3$), 6.93 (s, 2H, Cp), 7.00 (m, 4H, Benzo), 7.74 (m, 4H, Benzo). ^{13}C NMR (benzene-d_6): δ 1.73 (Si*Me*$_3$), 119.31, 126.49, 133.18, 138.29 (Cp/Benzo). One Cp/Benzo resonance not located.

Preparation of (η^5-C_9H_5-1,3-$(CHMe_2)_2)_2HfCl_2$ (2-Cl_2). This molecule was prepared in a similar manner to **1-Cl_2** with 2.05 g (9.94 mmol) of Li[C_9H_5-1,3-$(CHMe_2)_2$] and 1.60 g (5.00 mmol) of $HfCl_4$, yielding 2.16 g (67%) of **2-Cl_2**. Anal. Calcd for $C_{30}H_{38}HfCl_2$: C, 55.60; H, 5.91. Found: C, 56.56; H, 3.78. ^{1}H NMR (benzene-d_6): δ 0.94 (d, 8 Hz, 12H, CH*Me*$_2$), 1.24 (d, 8 Hz, 12H, CH*Me*$_2$), 2.98 (m, 4H, C*H*Me$_2$), 6.76 (s, 2H, Cp), 6.91 (m, 4H, Benzo), 7.24 (m, 4H, Benzo). ^{13}C NMR (benzene-d_6): δ 20.74, 25.42, 25.62 ($CHMe_2$), 123.69, 125.04, 125.85, 125.95 (Cp/Benzo). One Cp/Benzo resonance not located.

Preparation of *rac/meso*-(η^5-C_9H_5-1-(^{i}Pr)-3-(Me))$_2$HfCl$_2$ (*rac/meso*-3-Cl_2). This molecule was prepared in a similar manner to **1-Cl_2** in a 100 mL round-bottom flask with 2.00 g (11.22 mmol) of Li[C_9H_5-1-^{i}Pr-3-Me], 1.80 g (5.61 mmol) of $HfCl_4$, and approximately 160 mL of diethyl ether. This yielded 2.34 g (72%) of yellow **3-Cl_2** as a mixture of *rac* and *meso* isomers. Anal. Calcd for $C_{26}H_{30}HfCl_2$: C, 52.76; H, 5.11. Found: C, 52.80; H, 4.77. ^{1}H NMR (benzene-d_6): δ 0.99 (d, 7 Hz, 6H, CH*Me*$_2$), 1.06 (d, 7 Hz, 6H, CH*Me*$_2$), 1.14 (d, 7 Hz, 12H, CH*Me*$_2$), 2.20 (s, 6H, *Me*), 2.21 (s, 6H, *Me*), 3.31 (m, 2H, C*H*Me$_2$) 3.52 (m, 2H, C*H*Me$_2$), 5.59 (s, 2H, Cp*H*), 5.67 (s, 2H, Cp*H*), 6.92 (m, 6H, Benzo), 7.01 (m, 2H, Benzo), 7.17 (m, 2H, Benzo), 7.23 (m, 2H, Benzo), 7.37 (m, 2H, Benzo), 7.44 (m, 2H, Benzo). ^{13}C{^{1}H} NMR (benzene-d_6): δ 12.47, 12.75 (*Me*), 21.26, 22.21, 24.91, 24.93, 27.25, 27.84 ($CHMe_2$), 100.22, 105.31, 109.49, 113.21, 117.95, 119.34, 121.11, 122.99, 123.60, 124.55, 124.77, 124.87, 124.99, 125.59, 126.75, 129.98 (Cp/Benzo). Two Cp/Benzo resonances not located.

Preparation of (η^5-C_9H_5-1-(^{i}Pr)-3-(Me))HfI$_3$ (4-I_3). A 100 mL round-bottom flask was charged with 1.70 g (2.87 mmol) of **2-Cl_2**, and approximately 60 mL of toluene was added. BI_3 (1.41 g, 3.59 mmol) was added slowly to the yellow solution, and the resulting mixture stirred for two days. The solvent was removed *in vacuo*, and the resulting brown solid washed with cold pentane, yielding 1.32 g (63%) of **4-I_3** instead of the desired diiodide species (**4-I_2**). ^{1}H NMR (benzene-d_6): δ 0.93 (d, 7 Hz, 3H, CH*Me*$_2$), 1.29 (d, 7 Hz, 3H, CH*Me*$_2$), 2.30 (s, 3H, *Me*), 3.70 (m, 1H, C*H*Me$_2$), 6.48 (s, 1H, Cp*H*), 6.75 (m, 2H, Benzo), 7.34 (m, 2H, Benzo).

Preparation of *rac/meso*-(η^5-C_9H_5-1-(^{i}Pr)-3-(Me))$_2$HfI$_2$ (*rac/meso*-3-I_2). A 100 mL round-bottom flask was charge with 0.921 g (1.26 mmol) of **4-I_3**, and approximately 30 mL of diethyl ether was added. The pale yellow solution was chilled in a liquid nitrogen cooled cold well for 20 min, 0.225 g (1.26 mmol) of Li[C_9H_5-1-(^{i}Pr)-3-(Me)] was added to the solution, and the resulting mixture was stirred for two days. The solvent was removed *in vacuo*, and the orange solid washed with pentane and subsequently extracted into toluene and filtered through Celite. Removal of the toluene *in vacuo* yielded 0.888 g (91%) of **3-I_2** as a yellow powder. Anal. Calcd for $C_{26}H_{30}HfI_2$: C, 40.30; H, 3.90. Found: C, 39.63; H, 3.40. ^{1}H NMR (benzene-d_6): δ 0.97 (d, 7 Hz, 6H, CH*Me*$_2$), 0.98 (d, 7 Hz, 6H, CH*Me*$_2$), 1.12 (d, 7 Hz, 6H, CH*Me*$_2$), 1.19 (d, 7 Hz, 6H, CH*Me*$_2$), 2.08 (s, 6H, *Me*), 2.28 (s, 6H, *Me*), 3.32 (m, 2H, C*H*Me$_2$) 3.95 (m, 2H, C*H*Me$_2$), 6.01 (s, 2H, Cp*H*), 6.42 (s, 2H, Cp*H*), 6.86 (m, 4H, Benzo), 6.92 (m, 4H, Benzo), 7.17 (m, 2H, Benzo), 7.28 (m, 2H, Benzo), 7.33 (m, 2H, Benzo), 7.43 (m, 2H, Benzo). ^{13}C{^{1}H} NMR (benzene-d_6): δ 12.73, 14.21 (*Me*), 21.28, 22.05, 25.53, 25.84, 27.73, 30.16 ($CHMe_2$), 106.85, 110.17, 122.91, 123.83, 124.15, 124.25, 124.99, 125.20, 125.50, 125.79, 126.48, 126.64, 126.92, 127.04, 127.29, 128.59 (Cp/Benzo). Two Cp/Benzo resonances not located.

Preparation of (η^6-C_9H_5-1,3-$(SiMe_3)_2$)(η^5-C_9H_5-1,3$(SiMe_3)_2$)-Hf(C_4H_8O) (1-THF). A 20 mL scintillation vial was charged with 3.56 g of mercury and approximately 3 mL of diethyl ether. To the stirring mixture was added 0.020 g (0.875 mmol) of sodium, and the slurry was stirred for 10 min to ensure amalgamation. A diethyl ether slurry (∼8 mL) containing 0.100 g (0.130 mmol) of **1-Cl_2** was then added followed by 0.250 g of THF. The resulting reaction mixture was stirred vigorously for 1 h. Filtration of the

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

(48) Davison, A.; Rakita, P. E. *J. Organomet. Chem.* **1970**, *23*, 407.

(49) Brady, E. D.; Overby, J. S.; Meredith, M. B.; Mussman, A. B.; Cohn, M. A.; Hanusa, T. P.; Yee, G. T.; Pink, M. *J. Am. Chem. Soc.* **2002**, *124*, 9556.

green solution through Celite followed by solvent removal *in vacuo* yielded a green foam. Recrystallization from pentane at −35 °C yielded 0.070 g (70%) of a green solid identified as **1-THF**. Anal. Calcd for $C_{34}H_{54}Si_4OHf$: C, 53.06; H, 7.07. Found: C, 53.12; H, 6.73. ^{1}H NMR (benzene-d_6): δ 0.27 (s, 18H, Si*Me*$_3$), 0.30 (s, 18H, Si*Me*$_3$), 0.74 (br, 4H, THF), 2.48 (br, 4H, THF), 3.62 (m, 2H, Benzo), 3.69 (s, 1H, Cp), 5.98 (s, 1H, Cp), 6.75 (m, 2H, Benzo), 6.86 (m, 2H, Benzo), 7.75 (m, 2H, Benzo). ^{13}C NMR (benzene-d_6): δ 1.38, 1.77 (Si*Me*$_3$), 24.08, 74.83 (THF), 83.70, 90.28, 103.86, 114.47, 118.44, 122.89, 125.11, 126.19, 135.91, 142.43 (Cp/Benzo).

Preparation of (η^6-C_9H_5-1,3($SiMe_3$)$_2$)(η^5-C_9H_5-1,3($SiMe_3$)$_2$)-Hf($C_4H_{10}O_2$) (1-DME). To a 20 mL scintillation vial with 0.119 g (0.155 mmol) of **1-THF** dissolved in approximately 6 mL of benzene was added dropwise 35 mL (0.031 mg, 0.34 mmol) of dimethoxyethane. The green solution was stirred for 90 min. Solvent removal *in vacuo* followed by recrystallization from diethyl ether at −35 °C yielded 0.50 g (48%) of **1-DME** as a green solid. Anal. Calcd for $C_{34}H_{56}Si_4O_2Hf$: C, 51.84; H, 7.17. Found: C, 51.39; H, 6.58. ^{1}H NMR (benzene-d_6): δ 0.23 (s, 18H, $SiMe_3$), 0.44 (s, 18H, $SiMe_3$), 1.49 (br s, 4H, OCH_2s), 3.53 (s, 6H, OCH_3), 3.91 (m, 2H, Benzo), 4.30 (s, 1H, Cp), 6.20 (m, 2H, Benzo), 6.72 (s, 1H, Cp), 6.79 (m, 2H, Benzo), 7.16 (s, 1H, Cp), 7.53 (m, 2H, Benzo). ^{13}C NMR (benzene-d_6): δ 1.92, 3.11 ($SiMe_3$), 68.19 (OCH_2), 69.12 (OCH_3), 118.46, 141.38 (Cp), 79.22, 105.02, 123.81, 125.54 (Benzo), 83.86, 107.86, 120.40, 137.28 (Benzo).

Characterization of [(η^5-C_9H_5-1,3-($SiMe_3$)$_2$)$_2$HfCl]$_2$Na$_2$(DME)$_3$ ([1-Cl]$_2$Na$_2$(DME)$_3$). ^{1}H NMR (benzene-d_6): δ 0.36 (s, 36H, $SiMe_3$), 0.46 (s, 36H, $SiMe_3$), 1.27 (br s, 18H, DME Me), 1.61 (br s, 12H, DME CH_2), 3.64 (s, 4H, Benzo), 6.10 (s, 2H, CpH), 6.61 (m, 4H, Benzo), 7.02 (m, 4H, Benzo), 7.73 (m, 4H, Benzo). One CpH resonance not located.

Preparation of [(η^5-C_9H_5-1,3-($SiMe_3$)$_2$)$_2$HfCl] (1-Cl). A 50 mL round-bottom flask was charged with 14.37 g (0.072 mol) of mercury, and approximately 10 mL of diethyl ether was added. To the stirring solution, 0.072 g (3.13 mmol) of sodium was added, and the slurry was stirred for 20 min to ensure amalgamation. A diethyl ether slurry (∼30 mL) containing 0.400 g (0.521 mmol) of **1-Cl$_2$** was then added. The resulting reaction mixture was stirred vigorously for 1.25 h. Filtration of the green solution through Celite followed by solvent removal *in vacuo* yielded a brown-green foam. Recrystallization from pentane at −35 °C yielded 70 mg (18%) of green crystals identified as **1-Cl**. Anal. Calcd for $C_{30}H_{46}Si_4HfCl$: C, 49.16; H, 6.33. Found: C, 48.88; H, 6.35. ^{1}H NMR (benzene-d_6): δ 5.72 ($\Delta\nu_{1/2} = 287$ Hz). EPR (toluene): $g_x = 1.98$, $g_y = 1.96$, $g_z = 1.70$.

Preparation of (η^5-C_9H_5-1,3($SiMe_3$)$_2$Hf-*cyclo*-O(CH_2)$_3$CH$_2$ (1-*cyclo*-O(CH_2)$_3$CH$_2$). A flame-dried thick-walled glass vessel was charged with 0.078 g (0.10 mmol) of **1-THF** dissolved in approximately 5 mL of benzene. On the vacuum line, the reaction vessel was degassed, and 91 Torr (0.49 mmol) of THF was admitted via a 100.1 mL calibrated gas bulb. The green solution was then heated in an oil bath for 3 days at 85 °C. Solvent was removed *in vacuo*, and the resulting yellow oil was identified as **1-*cyclo*-O(CH_2)$_3$CH$_2$**. Attempts to recrystallize the compound as a solid have been unsuccessful for elemental analysis. ^{1}H NMR (benzene-d_6): δ 0.35 (s, 18H, Si*Me*$_3$), 0.41 (s, 18H, Si*Me*$_3$), 0.74 (m, 2H, $OCH_2CH_2CH_2CH_2$), 0.80 (m, 2H, $OCH_2CH_2CH_2CH_2$), 1.52 (m, 2H, $OCH_2CH_2CH_2CH_2$), 3.87 (t, 5 Hz, 2H, $OCH_2CH_2CH_2CH_2$), 6.01 (s, 2H, Cp*H*), 6.96 (m, 2H, Benzo), 7.12 (m, 2H, Benzo), 7.60 (m, 2H, Benzo), 7.81 (m, 2H, Benzo). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.36, 1.58 (Si*Me*$_3$), 27.49 ($OCH_2CH_2CH_2CH_2$), 32.61 ($OCH_2CH_2CH_2CH_2$), 46.31 ($OCH_2CH_2CH_2CH_2$), 73.63 ($OCH_2CH_2CH_2CH_2$), 83.41, 103.52, 123.81, 124.67, 126.28, 126.82, 132.71, 137.24, 138.31 (Cp/Benzo).

Characterization of (η^5-C_9H_5-1,3-($SiMe_3$)$_2$)(η^5-C_9H_5-η^1-1-$SiMe_3$-3-$SiMe_2CH_2$)]HfH (1-CMH). ^{1}H NMR (benzene-d_6): −2.23 (d, 12 Hz, 1H, Zr-C*H*$_2$), −1.98 (d, 12 Hz, 1H, Zr-C*H*$_2$), 0.20 (s, 9H, Si*Me*$_3$), 0.23 (s, 9H, Si*Me*$_3$), 0.39 (s, 9H, Si*Me*$_3$), 0.45 (s, 3H, Si*Me*$_2$CH$_2$), 0.62 (s, 3H, Si*Me*$_2$CH$_2$), 6.76 (s, 1H, Cp*H*), 6.79 (m, 2H, Benzo), 6.84 (m, 2H, Benzo), 7.39 (m, 1H, Benzo), 7.41 (m, 1H, Benzo), 7.71 (m, 2H, Benzo), 7.84 (s, 1H, Cp*H*), 13.26 (s, 1H, Zr-*H*). ^{13}C{^{1}H} NMR (benzene-d_6): δ −2.66, −1.03, −0.79, 1.23, 1.83 (Si*Me*$_3$/Si*Me*$_2$), 34.38 (Zr-CH$_2$), 91.22, 113.73, 114.88, 118.07, 121.65, 122.47, 123.04, 123.27, 124.05, 125.04, 125.15, 125.81, 126.48. Five Cp/Benzo resonances not located.

Preparation of (η^5-C_9H_5-1,3-($SiMe_3$)$_2$)$_2$Hf(CO)$_2$ (1-(CO)$_2$). A small thick walled glass vessel was charged with 0.080 g of **1-THF** and approximately 10 mL of pentane. The contents of the vessel were cooled to −196 °C and evacuated. At this temperature, 1 atm of CO was admitted. The resulting reaction mixture was warmed to ambient temperature and stirred for two days, during which time the dark green solution turned black. The contents of the vessel were cooled again, and the excess CO and solvent were removed *in vacuo*, yielding a dark foam. Recrystallization from pentane at −35 °C yielded 0.070 g (89%) of **1-(CO)$_2$** as a forest green solid. Anal. Calcd for $C_{32}H_{46}Si_4O_2Hf$: C, 51.00; H, 6.15. Found: C, 50.69; H, 5.87. ^{1}H NMR (benzene-d_6): δ 0.31 (s, 36 H, Si*Me*$_3$), 5.69 (s, 2H, Cp), 6.79 (m, 3.2 Hz, 4H, Benzo), 7.24 (m, 3.2 Hz, 4H, Benzo). ^{13}C NMR (benzene-d_6): δ 1.16 ($SiMe_3$), 94.24, 103.93, 124.73, 125.61, 126.94 (Cp/Benzo), 258.65 (Hf-CO). ν(CO) (pentane) = 1863, 1871, 1888, 1948, 1956, 1971 cm^{-1}.

Preparation of (η^5-C_9H_5-1,3-($CHMe_2$)$_2$Hf(CO)$_2$ (2-(CO)$_2$). A thick walled glass vessel was charged with 0.264 g (0.407 mmol) of **2-Cl$_2$** and 0.115 g (4.07 mmol) of activated Mg powder. On the high-vacuum line, approximately 15 mL of THF was vacuum transferred onto the solids, and the resulting slurry frozen in liquid nitrogen. One atmosphere of carbon monoxide was added to the vessel at −196 °C. The vessel was thawed and then placed in a 45 °C oil bath for one day. The CO atmosphere and the solvent were then removed *in vacuo*, leaving a green residue. The vessel was taken into the drybox, and the residue extracted into pentane. Filtration through Celite followed by solvent removal and recrystallization from pentane at −35 °C afforded **2-(CO)$_2$** along with unreacted **2-Cl$_2$**. ^{1}H NMR (benzene-d_6): δ 0.95 (d, 7 Hz, 12H, CH*Me*$_2$), 1.03 (d, 7 Hz, 12H, CH*Me*$_2$), 2.32 (m, 4H, C*H*Me$_2$), 5.18 (s, 2H, Cp*H*), 6.73 (m, 4H, Benzo), 7.00 (m, 4H, Benzo). ^{13}C NMR (benzene-d_6): δ 21.22, 25.73, 25.94 ($CHMe_2$), 96.92, 107.82, 112.46, 122.33, 122.96 (Cp/Benzo), 281.95 (Hf-CO). ν(CO) (pentane) = 1849, 1944 cm^{-1}.

Preparation of *rac/meso*-(η^5-C_9H_5-1-Me-3-$CHMe_2$Hf(CO)$_2$ (*rac/meso*-3-(CO)$_2$). A thick walled glass bomb was charged with 2.85 g (14.21 mmol) of mercury and approximately 3 mL of toluene in a nitrogen drybox. While stirring, 14 mg (0.61 mmol) of sodium metal was added, and the resulting amalgam was stirred for 20 min. A toluene solution of 80 mg (0.103 mmol) of **3-Cl$_2$** was added. The reaction vessel was attached to the vacuum line, and 1 atm of CO was added at −196 °C. The vessel was warmed to room temperature and stirred for 15 h. The excess CO was removed *in vacuo* and brought into the drybox. Filtration through Celite followed by solvent removal and recrystallization from pentane at −35 °C yielded 0.045 g (75%) of ***rac/meso*-3-(CO)$_2$** as a forest green solid in a 2 to 1 ratio. Anal. Calcd for $C_{28}H_{30}O_2Hf$: C, 58.28; H, 5.24. Found: C, 57.99; H, 5.46. ^{1}H NMR (benzene-d_6): δ 1.05 (d, 8 Hz, 3H, minor CH*Me*$_2$), 1.08 (d, 8 Hz, 3H, major CH*Me*$_2$), 1.12 (d, 8 Hz, 3H, minor CH*Me*$_2$), 1.13 (d, 8 Hz, 3H, major CH*Me*$_2$), 1.90 (s, 3H, major *Me*), 1.98 (s, 3H, minor *Me*), 2.48 (m, 1H, minor C*H*Me$_2$), 2.63 (m, 1H, major C*H*Me$_2$), 4.55 (s, 2H, major Cp*H*), 4.79 (s, 2H, minor Cp*H*), 6.71 (m, 8H, major/minor Benzo), 6.94 (m, 2H, major Benzo), 7.01 (m, 2H, minor Benzo), 7.09 (m, 2H, major Benzo), 7.17 (m, 2H, minor Benzo). ^{13}C NMR (benzene-d_6): δ 12.14, 12.17 (*Me*), 22.41, 22.98, 25.47, 25.74, 26.74, 27.38

(CHMe$_2$), 93.81, 99.27, 99.59, 108.24, 112.26, 115.21, 122.06, 122.23, 122.34, 122.64, 122.67, 122.75, 123.16, 123.57, 125.64, 128.51, 129.28 (Cp/Benzo), 271.71, 274.12 (Hf-CO). One Cp/Benzo and one Hf-CO resonance not located. ν(CO) (pentane) = 1871, 1864, 1961, 1948 cm^{-1}.

Dimethoxyethane Cleavage from 1-DME. A J. Young NMR tube was charged with 0.010 g (0.013 mmol) of **1-DME** dissolved in approximately 0.5 mL of benzene-d_6 and was allowed to sit at room temperature, and the reaction monitored over two days via NMR spectroscopy. Reaction resulted in cleavage of the dimethoxyethane to give a yellow solution of **1-OMe$_2$** and **1-C$_4$H$_8$**.

Characterization of (η^5-C$_9$H$_9$-1,3-(SiMe$_3$)$_2$)$_2$Hf(OMe)$_2$ (1-OMe$_2$). ^{1}H NMR (benzene-d_6): δ 0.25 (s, 36H, Si*Me*$_3$), 3.64 (s, 6H, O*Me*), 6.71 (s, 2H, Cp), 7.17 (m, 4H, Benzo), 7.72 (m, 4H, Benzo). ^{13}C NMR (benzene-d_6): δ −0.03 (Si*Me*$_3$), 78.85 (O*Me*), 114.00, 123.20, 124.64, 141.29, 141.68 (Cp/Benzo).

Preparation of (η^5-C$_9$H$_9$-1,3-(SiMe$_3$)$_2$)$_2$Hf(C$_4$H$_8$) (1-cyclo-C$_4$H$_8$). A J. Young NMR tube was charged with 0.020 g (0.026 mmol) of **1-THF**, and approximately 0.5 mL of benzene-d_6 was added. The tube was submerged in a −196 °C bath, and excess (approximately 250 Torr) ethylene was admitted. A rapid color change from green to yellow was observed upon thawing. Removal of the excess ethylene *in vacuo* and recrystallization in pentane afforded 10 mg of a yellow solid identified as **1-*cyclo*-C$_4$H$_8$**. Anal. Calcd for C$_{34}$H$_{54}$Si$_4$Hf: C, 54.19; H, 7.22. Found: C, 53.91; H, 7.20. ^{1}H NMR (benzene-d_6): δ 0.33 (s, 36H, Si*Me*$_3$), 0.39 (m, 4H, Hf−C*H*$_2$), 1.63 (m, 4H, Hf-CH$_2$C*H*$_2$), 6.32 (s, 2H, Cp), 7.17 (m, 4H, Benzo), 7.77 (m, 4H, Benzo). ^{13}C NMR (benzene-d_6): δ 1.58 (Si*Me*$_3$), 28.91 (Hf-CH$_2$*C*H$_2$), 57.62 (Hf-*C*H$_2$CH$_2$) 115.80, 122.90, 125.31, 130.64, 136.97 (Cp/Benzo).

Preparation of (η^5-C$_9$H$_5$-1,3(SiMe$_3$)$_2$)((η^5, η^3-C$_9$H$_6$-1,3(SiMe$_3$)$_2$)-HfH. (1-DHID-H). A thick walled glass vessel was charged with 0.055 g (0.072 mmol) of **1-THF** and approximately 10 mL of pentane. The contents of the vessel were frozen in liquid nitrogen, the vessel was evacuated, and 1 atm of dihydrogen was added. After thawing, the solution immediately changed color from a dark forest green to light yellow. The volatiles were removed *in vacuo*, and the residue was recrystallized from pentane to yield 0.042 g (83%) of a flaky tan solid identified as **1-DHID-H**. Anal. Calcd for C$_{30}$H$_{48}$Si$_4$Hf: C, 51.51; H, 6.92. Found: C, 51.12; H, 6.51. ^{1}H NMR (benzene-d_6): δ 0.29 (s, 9H, SiMe$_3$), 0.31 (s, 9H, SiMe$_3$), 0.32 (s, 9H, SiMe$_3$), 0.44 (s, 9H, SiMe$_3$), 2.32 (d, 12 Hz, 1H, CH$_2$), 2.51 (m, 1H, CH$_2$), 2.91 (br, 1H, allyl CH), 3.03 (s, 1H, Hf−H), 4.68 (m, 1H, allyl CH), 5.24 (d, 1H, 6.4 Hz, allyl CH), 5.84 (s, 1H, Cp), 6.85 (m, 2H, benzo), 6.95 (s, 1H, Cp), 7.25 (m, 1H, benzo), 7.56 (m, 1H, benzo). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.20, 1.42, 2.14, 2.67 (Si*Me*$_3$), 22.49 (*C*H$_2$), 37.61 (allyl *C*H), 95.44, 99.70, 102.82, 103.46, 105.86, 109.39, 109.45, 116.98, 123.58, 123.74, 124.68, 125.36, 125.97, 126.51, 126.92, 126.98 (Cp/Benzo).

Preparation of (η^5-C$_9$H$_9$-1,3-(SiMe$_3$)$_2$)$_2$HfH$_2$ (1-THI). A J. Young NMR tube was charged with 0.015 g (0.021 mmol) of **1-DHID-H** and approximately 0.5 mL of benzene-d_6. The contents of the tube were heated at 65 °C for 1 week. No significant color change was observed. ^{1}H NMR (benzene-d_6): 0.28 (s, 36H, Si*Me*$_3$), 1.73 (m, 4H, anti to Hf THI), 2.10 (m, 4H, syn THI), 2.75 (m, 4H, anti THI), 2.84 (m, 4H, syn THI), 5.82 (s, 2H, Cp*H*), 14.95 (s, 2H, Hf-*H*). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.36 (Si*Me*$_3$), 23.95, 27.86 (THI), 111.87, 117.55, 137.10 (Cp).

Preparation of (η^5-C$_9$H$_5$-1,3(SiMe$_3$)$_2$)$_2$HfH$_2$. (1-H$_2$). A 20 mL scintillation vial was charged with 0.240 g (0.312 mmol) of **1-Cl$_2$** and dissolved in approximately 5 mL of toluene. The yellow solution was chilled at −35 °C for 20 min, and 0.656 mL (0.656 mmol) of a 1.0 molar solution of sodium triethylborylhydride in toluene was syringed in. The resultant amber solution was stirred for 3 h, and the solvent removed *in vacuo*. The residue was taken into pentane and extracted through Celite, and the solvent removed *in vacuo*. Recrystallization from pentane at −35 °C afforded 0.081 g (37%) of a white crystalline solid identified as **1-H$_2$**. Anal. Calcd for C$_{30}$H$_{48}$Si$_4$Hf: C, 51.51; H, 6.92. Found: C, 51.23; H, 6.96. ^{1}H NMR (benzene-d_6): δ 0.31 (s, 18H, SiMe$_3$), 6.78 (m, 4H, Benzo), 7.25 (m, 4H, Benzo), 7.53 (s, 2H, Cp*H*), 14.85 (s, 1H, Zr-*H*). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.31 (Si*Me*$_3$), 110.36, 124.31, 126.21, 127.52, 131.56 (Cp/Benzo).

Preparation of (η^5-C$_9$H$_5$-1,3(SiMe$_3$)$_2$)$_2$Hf(H)(C$_6$N$_2$H$_9$) (1-DMAP). A 20 mL scintillation vial was charged with 0.058 g (0.075 mmol) of **1-THF**, 0.009 g (0.074 mmol) of 4-dimethylaminopyridine, and 10 mL pentane. The resulting solution was stirred overnight and changed color from dark green to white. The volatile components were removed *in vacuo*. Recrystallization of the resulting solid from pentane at −35 °C yielded 0.055 g (89%) of a fluffy white solid identified as **1-DMAP**. Anal. Calcd for C$_{30}$H$_{46}$Si$_4$HfN$_2$: C, 54.21; H, 6.89. Found: C, 54.00; H, 6.35. ^{1}H NMR (benzene-d_6): δ 0.47 (s, 18H, Si*Me*$_3$), 0.48 (s, 18H, Si*Me*$_3$), 2.35 (s, 6H, N*Me*$_2$), 4.96 (s, 2H, Cp), 5.84 (d, 4.8 Hz, 1H, DMAP), 6.69 (m, 4H, Benzo), 6.93 (s, 1H, Hf−H), 7.09 (s, 1H, DMAP), 7.28 (m, 7.2 Hz, 4H, Benzo), 7.68 (d, 6 Hz, 1H, DMAP). ^{13}C NMR (benzene-d_6): δ 2.00, 2.02 (Si*Me*$_3$), 39.15 (N*Me*$_2$), 108.41 (DMAP), 111.44 (DMAP), 123.38, 123.65, 125.09, 125.57 (Benzo), 124.81 (Cp), 144.99 (DMAP).

Preparation of ((η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)$_2$Hf(N$_2$CPh$_2$)(THF) (1-N$_2$CPh$_2$(THF)). A 20 mL scintillation vial was charged with 0.040 g (0.059 mmol) of **1-THF** and 0.012 g (0.062 mmol) of diphenyldiazomethane, and approximately 5 mL of pentane was added. The reddish-brown solution was stirred for 3 h, after which the solvent was removed *in vacuo*. Recrystallization in pentane afforded 0.010 g (19%) of an orange solid identified as **1-N$_2$CPh$_2$(THF)**. In benzene-d_6 solution, the compound is reddish-orange. Anal. Calcd for C$_{47}$H$_{64}$Si$_4$HfN$_2$O: C, 58.57; H, 6.69; N, 2.91. Found: C, 58.22; H, 6.35; N, 2.83. ^{1}H NMR (benzene-d_6): 0.42 (s, 18H, Si*Me*$_3$), 0.53 (s, 18H, Si*Me*$_3$), 1.10 (m, 2H, THF), 1.94 (m, 4H, THF), 2.99 (m, 2H, THF), 6.85 (m, 4H, Benzo/Ph), 6.99 (m, 2H, Benzo/Ph), 7.11 (m, 2H, Benzo/Ph), 7.27 (m, 4H, Benzo/Ph), 7.31 (s, 2H, Cp*H*), 7.36 (m, 2H, Benzo/Ph), 7.95 (m, 2H, Benzo/Ph), 8.12 (m, 2H, Benzo/Ph). ^{13}C{^{1}H} NMR (benzene-d_6): δ 0.61, 1.29 (Si*Me*$_3$), 25.72, 77.71 (Hf-THF), 107.87, 121.13, 121.20, 121.96, 122.72, 126.41, 126.47, 127.02, 127.48, 130.58, 139.59, 140.15, 140.85, 141.47, 142.58, 150.97 (Cp/Benzo). Two Cp/Benzo resonances not located.

Preparation of ((η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)$_2$Hf(NHN=CPh$_2$)H (1-(NHN=CPh$_2$)H). A flame-dried thick walled glass reaction vessel was charged with 0.037 g (0.038 mmol) of **1-N$_2$CPh$_2$(THF)**, and approximately 3 mL of pentane was added. While attached to the high-vacuum line, the contents of the vessel were frozen at −196 °C and evacuated. At this temperature, 1 atm of dihydrogen was admitted. After thawing, the resulting orange solution was stirred vigorously for 2 h, after which time the solvent was removed *in vacuo*, resulting in an orange solid. Recrystallization from pentane at −35 °C yielded 33 mg (94%) of an orange solid identified as **1-(NHN=CPh$_2$)H**. Anal. Calcd for C$_{43}$H$_{58}$Si$_4$HfN$_2$: C, 57.78; H, 6.54; N, 3.13. Found: C, 57.53; H, 6.43; N, 2.84. ^{1}H NMR (benzene-d_6): δ 0.42 (s, 18H, Si*Me*$_3$), 0.45 (s, 18H, Si*Me*$_3$), 6.22 (br s, 1H, N*H*), 6.53 (m, 4H, Benzo/Ph), 6.89 (m, 2H, Benzo/Ph), 7.08 (m, 2H, Benzo/Ph), 7.12 (s, 2H, Cp*H*), 7.18 (m, 2H, Benzo/Ph), 7.26 (m, 4H, Benzo/Ph), 7.52 (m, 2H, Benzo/Ph), 7.68 (m, 2H, Benzo/Ph), 9.31 (s, 1H, Hf-*H*). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.95, 1.98 (Si*Me*$_3$), 93.99, 122.47, 123.77, 123.86, 124.13, 125.15, 125.88, 126.29, 126.72, 126.97, 127.22, 129.11, 130.47, 131.52, 135.71, 139.40, 145.38 (Cp/Benzo). One Cp/Benzo resonance not located. IR (KBr): ν(*NH*) = 3320 cm^{-1}; ν(*ND*) = 2467 cm^{-1}.

Preparation of (η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)(η^5-C$_9$H$_5$-η^1-1-SiMe$_3$-3-SiMe$_2$CH$_2$)]Hf(NHN=CPh$_2$) (1-CM(NHN=CPh$_2$)). A J. Young NMR tube charged with 0.008 g (0.01 mmol) of **1-THF** and 0.002 g (0.01 mmol) of diphenyldiazomethane dissolved in approximately 0.5 mL of benzene-d_6 was heated at 65 °C for one day, resulting in a color change from red-orange to orange and was identified as **1-CM(NHN═CPh$_2$)**. Attempts to recrystallize as a solid have been unsuccessful for elemental analysis. ^{1}H NMR (benzene-d_6): δ −1.86 (d, 12 Hz, 1H, Zr-C*H*$_2$), −0.67 (d, 12 Hz, 1H, Zr-C*H*$_2$), 0.23 (s, 9H, Si*Me*$_3$), 0.36 (s, 9H, Si*Me*$_3$), 0.51 (s, 9H, Si*Me*$_3$), 0.72 (s, 3H, Si*Me*$_2$), 0.77 (s, 3H, Si*Me*$_2$), 4.65 (s, 1H, N-*H*), 6.46 (m, 1H, Benzo/Ph), 6.78 (m, 2H, Benzo/Ph), 6.89 (m, 4H, Benzo/Ph), 7.02 (m, 3H, Benzo/Ph), 7.13 (m, 3H, Benzo/Ph), 7.39 (s, 1H, Cp*H*), 7.70 (m, 3H, Benzo/Ph), 7.77 (s, 1H, Cp*H*), 7.78 (m, 1H, Benzo/Ph), 7.95 (m, 1H, Benzo/Ph). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.50, 1.61, 1.83, 1.92, 2.05 (Si*Me*$_3$/Si*Me*$_2$), 33.00 (Zr-*C*H$_2$), 104.63, 105.56, 110.47, 111.81, 117.42, 123.65, 123.69, 124.77, 125.78, 126.46, 128.94, 129.42, 129.44, 129.46, 129.49, 130.56, 130.58, 130.60, 135.57, 136.44, 137.26, 139.72, 144.24 (Benzo/Cp/Ph). Four Benzo/Cp/Ph resonances not located. IR (KBr): $\nu(NH)$ = 3290 cm^{-1}.

Preparation of ((η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)$_2$Zr(N$_2$CPh$_2$)(THF) (5-N$_2$CPh$_2$(THF)). This compound was prepared in a similar manner to **1-N$_2$CPh$_2$(THF)** in a J. Young NMR tube with 0.020 g (0.030 mmol) of **5-THF**, 0.006 g (0.031 mmol) of diphenyldiazomethane, and approximately 0.5 mL of benzene-d_6. The resulting reddish-brown solution was identified as **5-N$_2$CPh$_2$(THF)**. This particular compound is unstable to vacuum, so no elemental analysis was obtained. ^{1}H NMR (benzene-d_6): δ 0.42 (s, 18H, Si*Me*$_3$), 0.49 (s, 18H, Si*Me*$_3$), 0.86 (m, 4H, THF), 2.14 (m, 4H, THF), 6.85 (m, 4H, Benzo/Ph), 6.94 (m, 2H, Benzo/Ph), 7.07 (m, 2H, Benzo/Ph), 7.21 (m, 4H, Benzo/Ph), 7.41 (s, 2H, Cp*H*), 7.51 (m, 2H, Benzo/Ph), 7.57 (m, 2H, Benzo/Ph), 7.83 (m, 2H, Benzo/Ph). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.22, 1.71 (Si*Me*$_3$), 26.03, 76.66 (Hf-THF), 111.15, 121.92, 122.95, 123.86, 124.04, 124.20, 125.70, 126.06, 126.67, 126.72, 129.41, 130.95, 133.89, 134.61, 136.63, 138.45 (Cp/Benzo/Ph). Two Cp/Benzo/Phenyl resonances not located.

Preparation of ((η^5-C$_9$H$_5$-1,3-(SiMe$_3$)$_2$)$_2$Zr(N$_2$CPh$_2$)H) (5-(NHNCPh$_2$)H). A thick walled glass vessel was flame-dried and charged with 0.156 g (0.230 mmol) of **5-THF**, and approximately 10 mL of pentane was added. Also to the vessel was added 0.045 g (0.232 mmol) of diphenyldiazomethane dissolved in 1 mL of pentane. The resulting reddish-brown solution of **5-N$_2$CPh$_2$(THF)** was stirred for 3 h. On the high-vacuum line, the contents of the vessel were frozen at −196 °C and then evacuated. At this temperature, 1 atm of dihydrogen was added. After thawing, the resulting yellow solution was stirred vigorously for 2 h, after which time the solvent was removed *in vacuo*, resulting in a yellow solid. Recrystallization from pentane at −35 °C yielded 65 mg (32%) of an yellow solid identified as **5-(NHN═CPh$_2$)H**. Anal. Calcd for C$_{43}$H$_{58}$Si$_4$ZrN$_2$: C, 57.78; H, 6.54; N, 3.13. Found: C, 57.30; H, 7.00; N, 3.34. ^{1}H NMR (benzene-d_6): δ 0.39 (s, 18H, Si*Me*$_3$), 0.50 (s, 18H, Si*Me*$_3$), 4.61 (s, 2H, Cp*H*), 5.35 (br s, 1H, N*H*), 5.57 (s, 1H, Zr-*H*), 6.61 (m, 2H, Benzo/Ph), 6.69 (m, 2H, Benzo/Ph), 7.01 (m, 2H, Benzo/Ph), 7.13 (m, 2H, Benzo/Ph), 7.19 (m, 2H, Benzo/Ph), 7.33 (m, 4H, Benzo/Ph), 7.64 (m, 2H, Benzo/Ph), 7.86 (m, 2H, Benzo/Ph). ^{13}C{^{1}H} NMR (benzene-d_6): δ 1.80, 1.92 (Si*Me*$_3$), 123.51, 123.55, 123.86, 124.94, 125.66, 126.06, 126.74, 127.22, 127.41, 129.20, 129.33, 129.59, 129.75, 129.91, 131.79, 138.08, 146.70, 147.76 (Cp/Benzo/Ph). IR (pentane): $\nu(NH)$ = 3303 cm^{-1}; $\nu(ND)$ = 2455 cm^{-1}.

Preparation of ((η^5-C$_9$H$_5$-1,3-(CHMe$_2$)$_2$Zr(η^2-N$_2$CPh$_2$)) (6-N$_2$CPh$_2$). This compound was prepared in a similar manner to **1-N$_2$CPh$_2$(THF)** with 0.084 g (0.171 mmol) of **6**, 0.033 g (0.170 mmol) of diphenyldiazomethane, and approximately 8 mL of pentane. Recrystallization from pentane at −35 °C yielded 28 mg (24%) identified as **6-N$_2$CPh$_2$**. Anal. Calcd for C$_{43}$H$_{48}$N$_2$Zr: C, 75.50; H, 7.07; N, 4.09. Found: C, 75.27; H, 6.84; N, 3.58. ^{1}H NMR (benzene-d_6): δ 0.93 (d, 8 Hz, 6H, CH*Me*$_2$), 0.98 (d, 8 Hz, 6H, CH*Me*$_2$), 1.05 (d, 8 Hz, 12H, CH*Me*$_2$), 2.66 (m, 2H, CH*Me*$_2$), 2.75 (m, 2H, CH*Me*$_2$), 6.64 (s, 2H, Cp*H*), 6.83 (m, 2H, Benzo/Ph), 6.92 (m, 2H, Benzo/Ph), 7.12 (m, 6H, Benzo/Ph), 7.23 (m, 6H, Benzo/Ph), 7.34 (m, 2H, Benzo/Ph), 8.31. ^{13}C{^{1}H} NMR (benzene-d_6): δ 20.93, 21.51, 24.57, 24.89, 25.34, 25.43 (CHMe$_2$), 115.70, 122.70, 122.76, 123.28, 124.07, 124.44, 124.65, 124.76, 125.11, 125.37, 125.88, 126.20, 128.45, 128.48, 128.66, 137.86, 141.01 (Cp/Benzo/Ph). One Cp/Benzo/Ph resonance not located.

Preparation of ((η^5-C$_9$H$_5$-1,3-(CHMe$_2$)$_2$Zr(N$_2$CPh$_2$)H) (6-(NHNCPh$_2$)H). This compound was prepared in a similar manner to **1-(NHN═CPh$_2$)H** using 0.053 g (0.077 mmol) of **6-N$_2$CPh$_2$**. Recrystallization from pentane at −35 °C yielded 33 mg (62%) identified as **6-(NHN═CPh$_2$)H**. Anal. Calcd for C$_{43}$H$_{50}$N$_2$Zr: C, 75.28; H, 7.35; N, 4.08. Found: C, 75.03; H, 7.61; N, 4.98. ^{1}H NMR (benzene-d_6): δ 1.25 (d, 8 Hz, 6H, CH*Me*$_2$), 1.28 (d, 8 Hz, 6H, CH*Me*$_2$), 1.32 (d, 8 Hz, 6H, CH*Me*$_2$), 1.34 (d, 8 Hz, 6H, CH*Me*$_2$), 3.45 (m, 4H, CH*Me*$_2$), 4.82 (s, 2H, Cp*H*), 5.58 (br s, 1H, N*H*/Zr-*H*), 5.79 (s, 1H, N*H*/Zr-*H*), 6.64 (m, 2H, Benzo/Ph), 6.73 (m, 2H, Benzo/Ph), 7.11 (m, 4H, Benzo/Ph), 7.26 (m, 4H, Benzo/Ph), 7.32 (m, 2H, Benzo/Ph), 7.38 (m, 2H, Benzo/Ph), 7.40 (m, 2H, Benzo/Ph), 8.05 (m, 2H, Benzo/Ph). ^{13}C{^{1}H} NMR (benzene-d_6): δ 22.78, 23.95, 24.80, 25.72, 27.97, 28.33 (CHMe$_2$), 110.24, 117.35, 118.90, 121.94, 122.31, 122.64, 123.07, 123.98, 126.52, 126.65, 127.83, 129.29, 129.91, 132.50, 138.50 (Cp/Benzo/Ph). One Cp/Benzo/Ph resonance not located. IR (pentane): $\nu(NH)$ = 3298 cm^{-1}. $\nu(ND)$ = 2448 cm^{-1}.

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Supporting Information Available: Crystallographic data for **1-THF**, **([1-Cl]$_2$Na$_2$(DME))$_2$**, and **1-Cl** in cif format, variable-temperature EPR data, and additional NMR spectra. This material may be accessed, free of charge, via the Internet at http://pubs.acs.org.

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