N_2 Hydrogenation Promoted by a Side-On Bound Hafnocene Dinitrogen Complex

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Reduction of the hafnocene diiodide $(\eta^5\text{-}C_5Me_4H)_2HfI_2$ with excess sodium amalgam under 1 atm of dinitrogen yielded the hafnocene dinitrogen complex $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$. X-ray diffraction has established a strongly activated, side-on bound, bridging N_2 ligand with an N−N bond length of 1.423(11) Å. Exposure of the dinitrogen compound to 1 atm of dihydrogen at 23 °C resulted in rapid hydrogenation of the N_2 ligand, affording the hydrido hafnocene diazenido complex $[(\eta^5\text{-}C_5Me_4H)_2HfH]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2H_2)$. Confirmation of N_2 hydrogenation has been provided by NMR and IR spectroscopic studies and X-ray diffraction. Pseudo-first-order observed rate constants for H_2 addition have been measured by monitoring the disappearance of a principally LMCT band centered at 886 nm $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$ as a function of time. The hafnocene complex hydrogenates dinitrogen approximately 4 times faster than the corresponding zirconocene compound. Divergent chemistry from zirconium is observed upon thermolysis of $[(\eta^5\text{-}C_5Me_4H)_2HfH]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2H_2)$, which results in cyclopentadienyl methyl group cyclometalation rather than N−N bond scission.

Introduction

Recently there has been renewed interest in the chemistry of group 4 transition-metal dinitrogen complexes, in part due to the diversity of transformations available to elaborate the N−N bond. Both in situ and isolated titanium dinitrogen complexes[1] have been used to prepare ammonia,[2,3] hydrazine, amines, and heterocycles,[4] principally through addition of electrophiles to coordinated N_2. Recently titanium-based dinitrogen functionalization has been extended to include nucleophilic attack, whereby a phosphine ligand is postulated to undergo addition to a transient, dianionic, bridging titanium dinitride, prepared from over-reduction of the corresponding N_2 compound.[5]

Zirconium dinitrogen chemistry has also proven versatile for N_2 elaboration, with observation of N_2 functionalization by both protic[6,7] and nonpolar reagents.[8] Work from our laboratory with substituted bis(cyclopentadienyl)zirconium complexes has demonstrated that tuning the metallocene steric and electronic environments allows synthesis of compounds with strongly activated, side-on-bound N_2 ligands.[9] These molecules undergo facile 1,2-addition of dihydrogen at ambient temperature to form hydrido zirconocene diazenido compounds and ultimately ammonia upon additional hydrogenation at 85 °C.[9] Both computational[10,11] and experimental[10,12] studies support a reaction pathway involving 1,2-addition of dihydrogen through an ordered transition structure with synchronous H−H bond breaking and Zr−H and N−H bond formation. This functionalization strategy has also been extended to include the addition of terminal alkynes to yield acetylido zirconocene diazenido complexes.[7]

While dinitrogen chemistry has been well studied for titanium and zirconium, that with hafnium is relatively underdeveloped. One reason for the paucity of hafnium dinitrogen complexes is the difficulty associated with reducing hafnium from its highest oxidation state.[13] For example, synthesis of $[(\eta^5\text{-}C_5Me_5)_2Hf(\eta^1\text{-}N_2)]_2(\mu_2,\eta^1{:}\eta^1\text{-}N_2)$[14] requires much more forcing conditions than for its zirconium congener,[6] relying on the reduction of bis(pentamethyl)hafnocene diiodide with sodium/potassium alloy. Similar observations have been made during the reduction of the bis(amido)bis(phosphine)hafnium dihalide derivatives

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[1] For representative examples see: (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087. (b) Duchateau, R.; Gambarotta, S.; Beydoun, N.; Bensimon, C. *J. Am. Chem. Soc.* **1991**, *113*, 8986. (c) Berry, D. H.; Procopio, L. J.; Caroll, P. J. *Organometallics* **1988**, *7*, 570. (d) Pez, G. P.; Apgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482. (e) De Wolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977. (f) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893. (g) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822. (h) Hanna, T. E.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14688. (i) Scherer, A.; Lützen, A.; Friedemann, M.; Haase, D.; Saak, W.; Beckhaus, R. *Eur. J. Inorg. Chem.* **2005**, 1003.

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Table 1. Metrical Data for 1-N_2, 1-N_2H_2, and Their Zirconium Congeners[a]

	1-N_2	$[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2\eta^2{:}\eta^2\text{-}N_2)$	**1-N_2H_4**	$[(\eta^5\text{-}C_5Me_4H)_2ZrH]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2H_2)$
M(1)−N(1)	2.072(3)	2.118(1)	2.1755(19)	2.3163(14)
M(1)−N(2)	2.089(4)	2.131(1)	2.295(2)	2.1974(13)
M(1A)−N(1)[b]	2.072(3)	2.119(1)	2.295(2)	2.1974(13)
M(1A)−N(2)	2.089(4)	2.131(1)	2.1755(19)	2.3163(14)
N(1)−N(2)	1.423(11)	1.3773(3)	1.467(4)	1.457(3)
N(1)−M(1)−N(2)	40.0(3)	37.81(9)	38.18(9)	37.55(6)
N(2)−N(1)−M(1A)	70.6(3)	71.57(7)	66.49(13)	75.66(9)
N(2)−N(1)−M(1)	70.6(3)	71.56(7)	75.33(14)	75.71(9)
M(1A)−N(1)−M(1)	141.2(5)	143.13(14)	120.84(8)	120.99(6)
N(1)−N(2)−M(1A)	69.4(3)	70.62(7)	66.49(13)	75.71(9)
dihedral angle[c]	65.3	65.0	69.7	69.5

[a] Distances are reported in Å and angles in deg. [b] In the structures of the diazenido hydride complexes, the nitrogen atoms are related by symmetry and are labeled N(1) and N(1A) in tables of bond distances and angles. [c] Angle defined as the dihedral angle formed between the planes defined by the cyclopentadienyl centroids and the metal center.

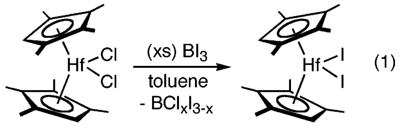
$(P_2N_2)HfX_2$ ($P_2N_2 = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$; X = Cl, I).[15] Whereas reduction of the dichloride complex with KC_8 furnishes a number of products, including the *P*-phenyl-bridged dimer $[(P_2N_2)Hf]_2$, only reduction of the corresponding diiodide yields the desired dinitrogen complex $[(P_2N_2)Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$.[15]

In this contribution, the synthesis of a reactive, side-on-bound hafnocene dinitrogen complex is described. This compound undergoes facile 1,2-addition of dihydrogen to form the corresponding hydrido hafnocene diazenido derivative, providing the first example of N_2 hydrogenation with hafnium. Both rate constants and kinetic isotope effects for the hydrogenation (deuteration) reaction have been determined and support a mechanistic pathway similar to that proposed for the corresponding zirconocene.[12] In chemistry divergent from zirconium, thermolysis of the hydrido hafnocene diazenido compound results in kinetically reversible and ultimately thermodynamically irreversible cyclometalation of the cyclopentadienyl methyl substituents with no evidence for cleavage of the N−N bond.

Results and Discussion

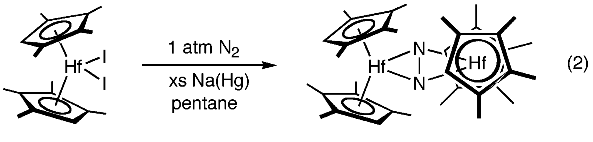
Preparation of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$ (1-N_2). The initial strategy explored to prepare the desired hafnocene dinitrogen complex followed the procedure described for the synthesis of $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$.[9] Stirring $(\eta^5\text{-}C_5Me_4H)_2HfCl_2$ (**1-Cl_2**)[16] with an excess (∼5 equiv) of 0.5% sodium amalgam or KC_8 in toluene or pentane afforded a mixture of diamagnetic products and remaining starting material. The major product has tentatively been identified as the hafnocene hydrido chloride complex $(\eta^5\text{-}C_5Me_4H)_2Hf(H)Cl$. This species most likely results from incomplete reduction of the hafnocene dichloride to transiently yield the corresponding monochloride, $[(\eta^5\text{-}C_5Me_4H)_2HfCl]_n$, which promotes hydrogen atom abstraction from either a cyclopentadienyl ligand or the solvent.

To overcome the problems associated with incomplete reduction and subsequent unwanted side reactions, a more labile hafnocene precursor was sought. Attempts to prepare the diiodide complex $(\eta^5\text{-}C_5Me_4H)_2HfI_2$ (**1-I_2**) by treatment of **1-Cl_2** with excess Me_3SiI yielded the mixed-halide derivative $(\eta^5\text{-}C_5Me_4H)_2Hf(I)Cl$. While extended reaction times and addition of more silyl iodide did result in further conversion, mixtures of products were continually obtained. Synthesis of the desired product was achieved by performing the iodination with excess BI_3 in toluene, furnishing the target diiodide, **1-I_2**, in 90% yield (eq 1).



1-Cl_2 **1-I_2** (90 %)

Reduction of the diiodide complex **1-I_2** with an excess of 0.5% sodium amalgam under 1 atm of dinitrogen for 2 days followed by filtration and recrystallization from pentane at −35 °C afforded the deep purple dinitrogen complex $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$ (**1-N_2**) in modest yield (eq 2). This compound can also be prepared by reduction of **1-I_2** with KC_8, although special care must be taken, as stirring the reaction mixture for longer than 24 h resulted in decomposition. The benzene-d_6 solution ^1H NMR spectrum of **1-N_2** at 23 °C exhibits three (two overlapping) broad cyclopentadienyl methyl resonances, consistent with a dynamic process on the NMR time scale. As was described previously for related zirconocene complexes,[12] this could either be a result of side-on−end-on interconversion of the N_2 ligand or a rocking of the cyclopentadienyl ligands in the dimer. Consistent with a symmetry-generating dynamic process, a single ^{15}N NMR resonance is observed at 590.5 ppm at this temperature, shifted slightly upfield from the value of 621.1 ppm reported for the zirconium congener.[9]



1-I_2 **1-N_2** (27 %)

In addition to NMR spectroscopy and combustion analysis, **1-N_2** was also characterized by single-crystal X-ray diffraction. A representation of the solid-state structure is presented in Figure 1, while selected metrical data are reported in Table 1. The corresponding data for the analogous zirconocene dinitrogen compound is also reported for comparison. The solid-state structure confirms a side-on-bound, strongly activated N_2 ligand with an N−N bond distance of 1.423(11) Å, slightly elongated from the value of 1.3773(3) Å observed in the zirconocene compound. Accordingly, the hafnium−nitrogen bond distances of 2.072(3) and 2.089(4) Å are contracted from the zirconocene values of 2.118(1) and 2.131(1) Å. As with the zirconium

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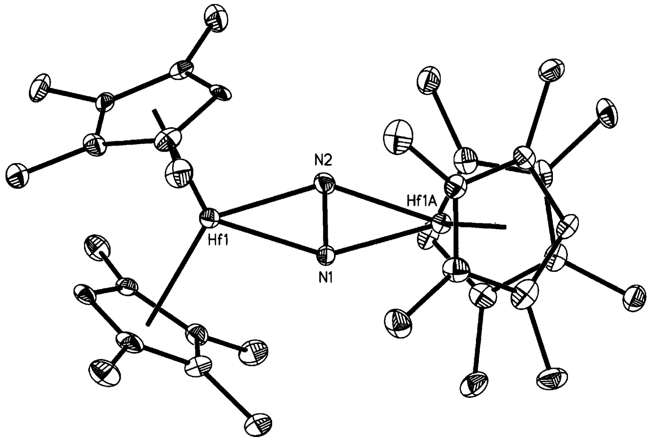
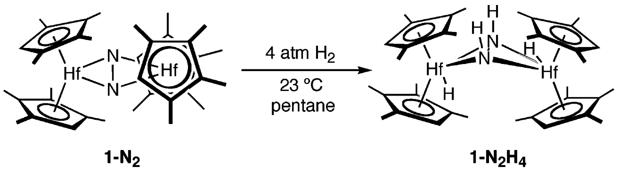


Figure 1. Molecular structure of **1-N_2** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

compound, **1-N_2** has a twisted dimeric structure with a comparable wedge dihedral angle of 65.3°. The lengthening of the N−N bond with concomitant contraction of the M−N bonds is consistent with greater N_2 reduction imparted by the more reducing third-row metal[13] and is indicative of greater contribution from the $[N_2]^{4-}$ canonical form in the overall resonance hybrid. This assertion is also supported by the "imido-like" character of the frontier molecular orbitals as determined by DFT calculations (see the Supporting Information).

Addition of 4 atm of H_2 to a pentane solution of **1-N_2** yielded a white solid identified as the hydrido hafnocene diazenido complex $[(\eta^5\text{-}C_5Me_4H)_2HfH]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2H_2)$ (**1-N_2H_4**) (eq 3).



(3)

The spectroscopic features of **1-N_2H_4** are diagnostic of dinitrogen hydrogenation.[9,12] A broad, upfield-shifted N−H ^1H NMR resonance is observed at 0.89 ppm for the $[N_2H_2]$ ligand and is consistent with side-on diazenido coordination.[7] Confirmation of the identity of the peak as an N−H bond has been provided by isotopic labeling experiments. This peak is absent in the ^1H NMR spectrum of the deuterated isotopologue **1-N_2D_4**, prepared by treatment of **1-N_2** with D_2 gas, but is observed by ^2H NMR spectroscopy at 0.80 ppm. In addition, this peak splits into an AA′XX′ pattern upon preparation of **1-$^{15}N_2H_4$** and cooling of a toluene-d_8 solution of the compound to −45 °C. An N−H stretch centered at 3297 cm^{-1} has also been observed in the solid-state (KBr) infrared spectrum of **1-N_2H_4**. This band shifts to 2446 cm^{-1} for **1-N_2D_4**. Observation of a single, upfield-shifted ^{15}N NMR resonance at 70.78 ppm at −45 °C is also consistent with a side-on-bound diazenido compound.[7] A sharp singlet is observed downfield at 8.15 ppm, assigned as the hafnium hydride resonance. This peak has also been confirmed by isotopic labeling.

As was observed with the corresponding zirconocene compound,[7,9] the cyclopentadienyl methyl groups and hydrogens appear as broad singlets at 23 °C. Warming a toluene-d_8 solution to 47 °C produced a spectrum with four sharp methyl signals and one cyclopentadienyl hydrogen, with no appreciable change in the location of the N−H and Hf−H peaks. Cooling this same solution to −40 °C resulted in the appearance of eight cyclopentadienyl methyl groups and two cyclopentadienyl hydrogens. The dynamic process could be a result of either inversion of the diazenido core[7] or rapid side-on−end-on interconversion of the $[N_2H_2]$ ligand. If the latter process is operative, appreciable amounts of the end-on isomer are not present in solution, as the chemical shift of the N−H resonance remains essentially constant as a function of temperature.[7]

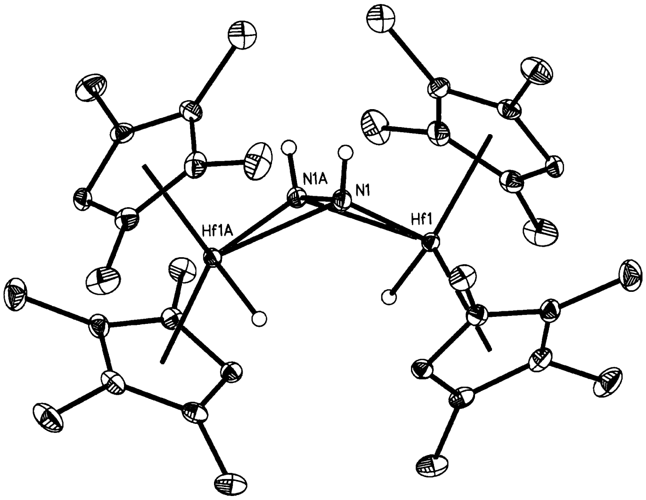


Figure 2. Molecular structure of **1-N_2H_4** with 30% probability ellipsoids. Hydrogen atoms, except for those attached to nitrogen and hafnium, are omitted for clarity.

Slow diffusion of dihydrogen into a saturated pentane solution of **1-N_2** furnished large single crystals suitable for X-ray diffraction. The solid-state structure is presented in Figure 2, while selected metrical parameters for this compound and its zirconocene congener are reported in Table 1. The data were of sufficient quality that all of the hydrogens were located and refined. As is typically observed in side-on bound group 4 metallocene diazenido complexes,[7,9] the molecule contains a pyramidalized $[N_2H_2]$ core and an elongated N−N bond of 1.467(4) Å. In general, the hafnium−nitrogen bonds are shorter than the corresponding zirconium−nitrogen bonds, consistent with the usual trend in moving from a second- to third-row transition metal.[13] Similar to the case for **1-N_2**, **1-N_2H_4** is twisted with a dihedral angle of 69.7°.

Kinetics and Mechanism of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$ Hydrogenation. The clean and quantitative conversion of **1-N_2** to **1-N_2H_4** prompted further investigation into the kinetics and mechanism of N_2 hydrogenation. Before rate data could be obtained, a reliable spectroscopic method for monitoring the conversion between the two molecules needed to be established. Previously, we reported that electronic spectroscopy is useful for determining the rate of hydrogenation of coordinated dinitrogen in zirconocene complexes. This technique is effective in part due to the ability to measure reasonably fast reaction rates and maintain efficient mixing of the gaseous dihydrogen with the solution containing the metallocene dinitrogen compound.[12]

The electronic spectrum of **1-N_2** in heptane solution (Figure 3) exhibits an intense band ($\epsilon = 6538$ M^{-1} cm^{-1}) centered at 886 nm, tentatively assigned as a principally ligand-to-metal charge transfer band, arising from a ground state with occupation of a HOMO compromised of the hafnium−dinitrogen backbond to an excited state that populates an orbital of essentially pure hafnium $1a_1$ parentage (see the Supporting Information). The observed 120 nm blue shift compared to the signal for the zirconocene complex[12] is consistent with the expectation of a higher energy electronic transition for a third-row versus a second-row transition metal.

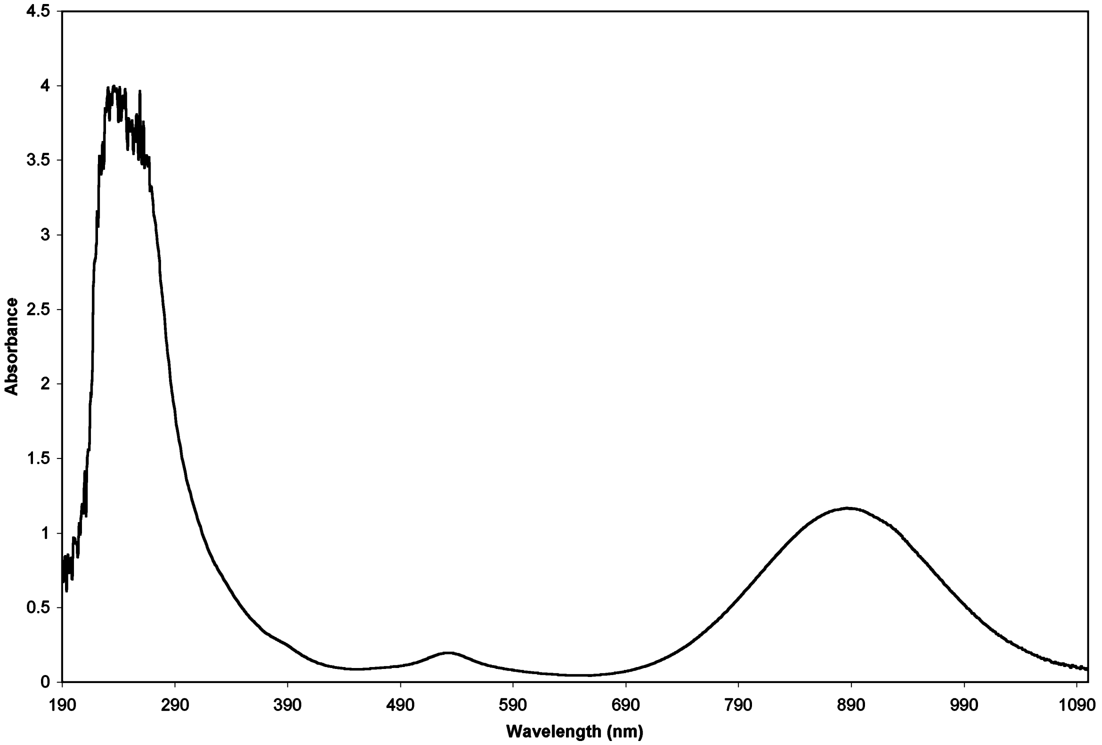


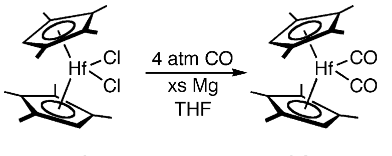
Figure 3. Electronic spectrum of **1-N$_2$** in heptane solution.

Table 2. Absorption Maxima (λ_{max}) and Extinction Coefficients (ϵ) for 1-N$_2$ and CO Stretching Frequencies of the Corresponding Metallocene Dicarbonyls

1-N$_2$		[(η^5-C$_5$Me$_4$H)$_2$Zr]$_2$(μ_2,η^2:η^2-N$_2$)	
λ_{max}[a]	ϵ	λ_{max}[a]	ϵ
		280	11700
		351	3700
553	381	648	
886	6538	1006	11400
1945[b]	1849[b]	1951[b]	1858[b]

[a] Values reported in nm. [b] ν(CO) stretching frequencies of the corresponding metallocene dicarbonyl complexes recorded in pentane solution. Values for the zirconocene are taken from ref 16.

Additional assessment of the relative electronic environments of the zirconocene and hafnocene [(η^5-C$_5$Me$_4$H)$_2$M] fragments has been provided by comparison of the CO stretching frequencies of the dicarbonyl derivatives. Magnesium reduction of **1-Cl$_2$** in THF solution in the presence of 4 atm of carbon monoxide furnished a white powder identified as (η^5-C$_5$Me$_4$H)$_2$Hf(CO)$_2$ (**1-(CO)$_2$**), albeit in modest (21%) yield (eq 4). Two strong carbonyl bands are observed at 1945 and 1849 cm^{-1} in the pentane solution infrared spectrum of **1-(CO)$_2$**, shifted to lower frequencies than for the corresponding zirconium complex, (η^5-C$_5$Me$_4$H)$_2$Zr(CO)$_2$ (Table 2).[17] Taken together, both the electronic and infrared spectroscopic data support a more reducing environment imparted by the hafnium center.



(4)

1-Cl$_2$ **1-(CO)$_2$** (27 %)

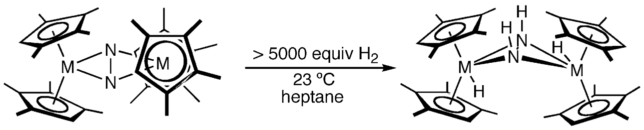


Figure 4. Relative rates of hydrogenation and kinetic isotope effects for the hydrogenation of zirconocene and hafnocene dinitrogen complexes.

With a reliable spectroscopic method in hand, rate constants for addition of dihydrogen to **1-N$_2$** were measured by monitoring the disappearance of the LMCT band centered at 886 nm. The product, **1-N$_2$H$_4$**, is transparent in this region. The experimental setup used for the kinetics measurements has been described previously,[12] and all runs were conducted with a 0.173 mM solution of metal complex with 0.693 atm of H$_2$. This pressure and volume of dihydrogen at 23 °C corresponds to greater than 5000 equiv of H$_2$, well above the acceptable minimum for pseudo-first-order conditions. Using this technique, a pseudo-first-order observed rate constant of [1.6(2)] $\times$ 10^{-2} s^{-1} was measured, 4.3 times *faster* than for the corresponding zirconium congener, which has an observed rate constant of [3.9(4)] $\times$ 10^{-3} under identical conditions (Figure 4).[12] This observation is in contrast to normal trends, where reactions such as olefin insertion into a metal hydride[18] are slower for hafnium than for zirconium.

A pseudo-first-order observed rate constant of [9.5(5)] $\times$ 10^{-3} has likewise been measured for D$_2$ addition to **1-N$_2$**, providing a normal primary kinetic isotope effect of 1.7(3) at 23 °C. A value with this direction and magnitude is consistent with a rate-determining 1,2-addition of dihydrogen (or dideuterium) to the dinitrogen complex proceeding through an ordered transition structure, where H−H bond scission is synchronous with Hf−H

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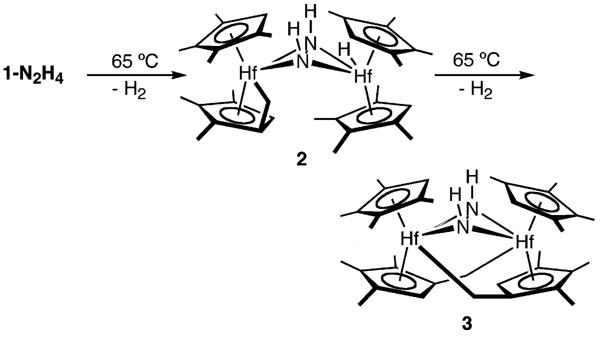
and N−H bond formation. Similar transition structures have been proposed for 1,2-additions of C−H bonds to group 4 imido complexes[19] as well as in dinitrogen hydrogenation reactions.[20] While the origin of the observed rate enhancement for N_2 hydrogenation upon moving from zirconium to hafnium remains speculative and is likely the result of many effects, one possibility is the increased imido character in the hafnium case, as judged by the metrical parameters determined from the solid-state structure of **1-N$_2$**.

Thermolysis of $[(\eta^5\text{-}C_5Me_4H)_2HfH]_2(\mu_2,\eta^2:\eta^2\text{-}N_2H_2)$. We have previously reported that continued hydrogenation of $[(\eta^5\text{-}C_5Me_4H)_2ZrH]_2(\mu_2,\eta^2:\eta^2\text{-}N_2H_2)$ at 85 °C affords small quantities of free ammonia and the zirconocene dihydride $(\eta^5\text{-}C_5Me_4H)_2ZrH_2$ as the primary organometallic product.[9] Other zirconocene products arising from the interaction of NH_3 with the zirconocene dihydride and hydrido zirconocene diazenido compound are also observed. To determine if **1-N$_2$H$_4$** was competent for ammonia synthesis, a heptane solution of the hydrido hafnocene diazenido complex was warmed to 90 °C under 4 atm of H_2. Collecting the volatiles and subsequent protonation with excess anhydrous HCl resulted in small quantities of NH_4Cl, as judged by ^1H NMR spectroscopy in DMSO-d_6 solution.[21] Dissolution of the remaining nonvolatile hafnium compound in benzene-d_6 and subsequent analysis by ^1H NMR spectroscopy revealed an intractable and complex mixture of products that have not been identified.

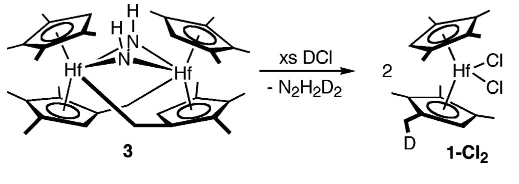
Because decomposition of the hafnocene was observed during ammonia synthesis, the thermal stability of **1-N$_2$H$_4$** in the absence of dihydrogen was studied in more detail. Warming a benzene-d_6 solution of **1-N$_2$H$_4$** to 65 °C for 24 h under an atmosphere of dinitrogen resulted in nearly complete consumption of the starting material with concomitant growth of a new hafnocene product identified as the cyclometalated hafnocene diazenido complex **2** (eq 5). The benzene-d_6 ^1H NMR spectrum of **2** exhibits 15 cyclopentadienyl methyl groups and 4 cyclopentadienyl hydrogens, consistent with a C_1-symmetric bimetallic hafnium compound. Evidence for cyclometalation is provided by the observation of two doublets centered at 1.05 and 1.35 ppm, assigned to the diastereotopic hydrogens on the methylene carbon bound to the hafnium. Confirmation of these assignments has been provided by COSY and $^1H-^{13}C$ HSQC NMR experiments. A single hafnium hydride is observed at 7.06 ppm, and doublets assigned to the N−H hydrogens on the diazenido core are found at 0.43 and 1.78 ppm. Assignment of the latter resonances has also been accomplished with the aid of two-dimensional NMR experiments. Unfortunately, the NMR data do not differentiate between cyclometalation on the same metal or across the dimer. Attempts to isolate **2** as a pure solid have been unsuccessful, as its formation is invariably accompanied by a second double-cyclometalated product (vide infra). It should be noted that evidence for reversible cyclometalation has been obtained with **1-N$_2$D$_4$**. Warming a benzene-d_6 solution of this compound to 45 °C resulted in isotopic exchange of the hafnium hydride and a cyclopentadienyl methyl group *prior* to the accumulation of significant quantities of **2**.



(5)

Continued thermolysis of **2** for days or warming **1-N$_2$H$_4$** to 110 °C on a preparative scale afforded a beige powder identified as the double-cyclometalated hafnocene diazenido complex **3** (eq 5). This molecule can also be prepared directly, albeit in lower purity, from thermolysis of **1-N$_2$**, demonstrating that direct 1,2-additions of C−H bonds[12] are also possible with this dinitrogen complex. As with **2**, the ^1H NMR spectrum of **3** exhibits diagnostic doublets centered at 0.97 and 1.41 ppm, assigned to the diastereopic hydrogens on the methylene carbon bound to the hafnium. In this case, higher symmetry is observed with a single N−H resonance centered at 1.41 ppm, along with 7 singlets for the cyclopentadienyl methyl groups. On the basis of these spectral features, combustion analysis, and degradation experiments (vide infra), the structure of **3** is formulated as the double-cyclometalated compound where the methylene hydrogens are bound to the adjacent hafnium in the dimer, similar to the case for the structurally characterized "mixed-ring" zirconocene examples.[12]

To confirm which cyclopentadienyl methyl group is cyclometalated, **3** was treated with an excess of deuterium chloride and the resulting hafnocene dichloride analyzed by ^2H NMR spectroscopy (eq 6). A single resonance centered at 1.79 ppm was observed by ^2H NMR spectroscopy. Performing a NOESY experiment on **1-Cl$_2$** identifies this methyl group as the one adjacent to the cyclopentadienyl hydrogen, indicating selective C−H activation of one of the methyl substituents. It should be noted that this methyl group also undergoes preferential cyclometalation in $(\eta^5\text{-}C_5Me_4H)_2ZrH_2$.[22]



(6)

Because cyclometalation from **1-N$_2$H$_4$** was observed at temperatures higher than those studied with the corresponding hydrido zirconocene diazenido compound, the thermolysis of the latter molecule was reinvestigated at 110 °C in benzene-d_6. Monitoring the reaction by ^1H NMR spectroscopy revealed a complex mixture of products, some of which exhibited diagnostic upfield doublets, indicative of diastereotopic methylene hydrogens of a cyclometalated methyl group. However, the number of products coupled with their low symmetry and, hence, large number of peaks prohibited definitive spectral assignment. Interestingly, treatment of this mixture with anhydrous DCl, added as a dioxane solution, quantitatively furnished the zirconocene dichloride $(\eta^5\text{-}C_5Me_4H\text{-}d)_2ZrCl_2$, with deuterium exclusively located in the cyclopentadienyl methyl group adjacent to the ring hydrogen, demonstrating the same cyclometalation preferences for the two different metals.

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Concluding Remarks

The first example of a side-on-bound hafnocene dinitrogen complex has been synthesized and crystallographically characterized. The metrical parameters of the dinitrogen complex as well as its electronic spectrum and vibrational stretching frequencies of the corresponding dicarbonyl derivative support a more reducing metal center than for the zirconocene congener. This behavior is a result of a more reducing third-row transition metal, a consequence of the greater thermodynamic driving force for these metals to attain their highest oxidation state. In other words, for the hafnocene dinitrogen complex, the diazenido canonical form, $[\mathrm{N_2}]^{4-}$, is a greater contributor to the overall hybrid than for zirconium. Interestingly, the observed rate constant for dihydrogen addition is approximately 4 times larger and may be a consequence of the increased imido character of the hafnium derivative. The kinetic isotope effect of $\mathrm{H_2}$ versus $\mathrm{D_2}$ addition supports a 1,2-addition pathway for dinitrogen functionalization, in agreement with the transition structure proposed in zirconium chemistry. 1,2-Addition of a carbon−hydrogen bond can also be used for N−H bond formation, yielding a double-cyclometalated dihafnium compound. In chemistry divergent from that for zirconium, this species is also obtained upon thermolysis of the hydrido hafnocene diazenido compound, perhaps due to a higher barrier for 1,2-elimination for the third-row transition metal.

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high-vacuum-line, Schlenk, or cannula techniques or in an M. Braun inert-atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[23] Toluene, benzene, pentane, and heptane were further dried by distillation from "titanocene".[24] Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Benzene-d_6 and toluene-d_8 were further dried by storage and distillation from "titanocene" immediately before use. Argon and hydrogen gas were purchased from Airgas Inc. and passed through a column containing manganese oxide on vermiculite and 4 Å molecular sieves before admission to the high-vacuum line. The hafnocene dichloride $(\eta^5\text{-}\mathrm{C_5Me_4H})_2\mathrm{HfCl_2}$ was prepared according to literature procedures.[16]

^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz (^{1}H) and 100.511 MHz (^{13}C). All chemical shifts are reported relative to $\mathrm{SiMe_4}$ using ^{1}H (residual) or ^{13}C NMR chemical shifts of the solvent as a secondary standard. ^{15}N NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 50.663 MHz, and chemical shifts were externally referenced to liquid ammonia. UV−vis spectra were recorded on a Hewlett-Packard 8543E spectrophotometer from 200 to 1100 nm with a diode array detector in heptane solution.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD area detector system equipped with a molybdenum X-ray tube ($\lambda = 0.710\,73$ Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Preparation of $(\eta^5\text{-}\mathbf{C_5Me_4H})_2\mathbf{HfI_2}$ (1-$\mathbf{I_2}$). A 100 mL flask was charged with 1.80 g (3.66 mmol) of $(\eta^5\text{-}\mathrm{C_5Me_4H})_2\mathrm{HfCl_2}$, 1.79 g (4.56 mmol) of $\mathrm{BI_3}$, and approximately 70 mL of toluene. The resulting reaction mixture was stirred for 3 days at ambient temperature, turning dark red after 1 day. The solvent was removed in vacuo, and the remaining yellow solid was washed with 30 mL of pentane and then dried under high vacuum overnight to yield 2.23 g (90%) of a yellow solid identified as **1-$\mathbf{I_2}$**. Anal. Calcd for $\mathrm{C_{18}H_{26}HfI_2}$: C, 32.04; H, 3.88. Found: C, 32.03; H, 3.74. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.76 (s, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.35 (s, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 5.19 (s, 2H, $\mathrm{C_5Me_4}\mathit{H}$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 15.74, 16.19 ($\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 110.60, 119.72 ($\mathit{C_5}\mathrm{Me_4H}$); one $\mathit{C_5}\mathrm{Me_4H}$ signal not located.

Preparation of $[(\eta^5\text{-}\mathbf{C_5Me_4H})_2\mathbf{Hf}]_2(\mu_2,\eta^2{:}\eta^2\text{-}\mathbf{N_2})$ (1-$\mathbf{N_2}$). A 20 mL scintillation vial was charged with 13.5 g (2.22 mmol) of 0.5% sodium amalgam and approximately 5 mL of toluene. The mixture was cooled to −35 °C, and 0.300 g (0.445 mmol) of **1-$\mathbf{I_2}$** was added. The resulting reaction mixture was stirred for 2 days at ambient temperature, turning dark purple after approximately 1 h. Following filtration through Celite, the filtrate was collected, the toluene was removed in vacuo, and the remaining dark purple solid was extracted with 20 mL of pentane and recrystallized at −35 °C to yield 0.051 g (27%) of purple crystals identified as **1-$\mathbf{N_2}$**. Anal. Calcd for $\mathrm{C_{36}H_{52}Hf_2N_2}$: C, 49.71; H, 6.03; N, 3.22. Found: C, 49.50; H, 5.80; N, 2.97. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.98 (bs, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.05 (bs, 12H, $\mathrm{C_5Me}$), 2.13 (bs, 24H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 5.49 (s, 4H, $\mathrm{C_5Me_4}\mathit{H}$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 11.70, 12.61, 12.83, 13.26 ($\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 108.78, 112.10, 115.61, 117.43, 122.21 ($\mathit{C_5}\mathrm{Me_4H}$). ^{15}N{^{1}H} NMR (benzene-d_6, 23 °C): δ 590.5.

Preparation of $[(\eta^5\text{-}\mathbf{C_5Me_4H})_2\mathbf{HfH}]_2(\mu_2,\eta^2{:}\eta^2\text{-}\mathbf{N_2H_2})$ (1-$\mathbf{N_2H_4}$). A thick-walled reaction vessel was charged with 0.031 g (0.036 mmol) of **1-$\mathbf{N_2}$** and approximately 20 mL of pentane. On a high-vacuum line, the vessel was submerged in liquid nitrogen and evacuated and 4 atm of dihydrogen was admitted. The contents of the vessel were warmed to ambient temperature, and the resulting reaction mixture was stirred overnight, forming a colorless mixture. The solvent and excess $\mathrm{H_2}$ were removed in vacuo, and the remaining solid was washed with pentane to yield 0.024 g (77%) of white powder identified as **1-$\mathbf{N_2H_4}$**. Anal. Calcd for $\mathrm{C_{36}H_{56}Hf_2N_2}$: C, 49.48; H, 6.46; N, 3.21. Found: C, 48.95; H, 6.57; N, 2.86. ^{1}H NMR (benzene-d_6, 23 °C): δ 0.89 (bs, 2H, N−H), 1.61 (bs, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.07 (bs, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.22 (s, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.32 (bs, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 5.21 (bs, 4H, $\mathrm{C_5Me_4}\mathit{H}$), 8.30 (s, 2H, Hf−$H$). ^{1}H NMR (toluene-$d_8$, 47 °C): δ 0.89 (s, 2H, N−H), 1.68 (s, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.07 (s, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.17 (s, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.28 (s, 12H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 5.13(s, 4H, $\mathrm{C_5Me_4}\mathit{H}$), 8.31 (s, 2H, Hf−$H$). ^{1}H NMR (toluene-$d_8$, −40 °C): δ 0.57 (s, 2H, N−H), 1.35 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.81 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.87 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.93 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.18 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.23 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.25 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 2.75 (s, 6H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 4.70 (s, 4H, $\mathrm{C_5Me_4}\mathit{H}$), 8.15 (s, 2H, Hf-$H$), 5.66 (s, 4H, $\mathrm{C_5Me_4}\mathit{H}$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 12.29, 12.98 ($\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 115.07 ($\mathit{C_5}\mathrm{Me_4H}$). ^{15}N{^{1}H} NMR (toluene-d_8, -45 °C): δ 70.78. IR (KBr): $\nu_{\mathrm{N-H}}$ 3297 cm^{-1}, $\nu_{\mathrm{N-D}}$ 2446 cm^{-1}, $\nu_{\mathrm{Hf-H}}$ 1604 cm^{-1}, $\nu_{\mathrm{Hf-D}}$ 1140 cm^{-1}.

Spectroscopic Identification of 2. A J. Young NMR tube was charged with approximately 10 mg of **1-$\mathbf{N_2H_4}$** and 0.5 mL of benzene-d_6. The sample was heated to 65 °C for 24 h and monitored by ^{1}H and ^{13}C NMR. ^{1}H NMR (benzene-d_6, 23 °C): δ 0.43 (d, 11.5 Hz, 1H, N−H), 1.05 (d, 11.3 Hz, 1H, Hf−CH_2), 1.35 (d, 11.3 Hz, 1H, Hf−CH_2), 1.78 (d, 11.5 Hz, 1H, N−H), 1.19 (s, 3H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.48 (s, 3H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.77 (s, 3H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.83 (s, 3H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.84 (s, 3H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.91 (s, 3H, $\mathrm{C_5}\mathit{Me_4}\mathrm{H}$), 1.92

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(s, 3H, $C_5\mathit{Me}_4H$), 1.98 (s, 3H, $C_5\mathit{Me}_4H$), 2.00 (s, 3H, $C_5\mathit{Me}_4H$), 2.01 (s, 3H, $C_5\mathit{Me}_4H$), 2.06 (s, 3H, $C_5\mathit{Me}_4H$), 2.11 (s, 3H, $C_5\mathit{Me}_4H$), 2.12 (s, 3H, $C_5\mathit{Me}_4H$), 2.14 (s, 3H, $C_5\mathit{Me}_4H$), 2.24 (s, 3H, $C_5\mathit{Me}_4H$), 4.85 (s, 1H, $C_5Me_4\mathit{H}$), 5.07 (s, 1H, $C_5Me_4\mathit{H}$), 5.88 (s, 1H, $C_5Me_4\mathit{H}$), 5.97 (s, 1H, $C_5Me_4\mathit{H}$), 7.06 (s, 1H, Hf−*H*). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 10.33, 11.63, 11.79, 11.91, 12.01, 12.15, 12.16, 12.31, 12.32, 12.64, 13.03, 13.38, 14.57, 14.70, 14.97 ($C_5\mathit{Me}_4H$), 32.28 (Hf−$\mathit{C}H_2$), 101.91, 103.77, 103.89, 106.07 (C_5Me_4H); quaternary carbon signals not located.

Preparation of [(η^5-C_5Me_4H)(η^5-C_5H_2-2,4-Me_2-1-η^1-CH_2)Hf]$_2$-(μ_2,η^2:η^2-N_2H_2) (3). A thick-walled reaction vessel was charged with 0.038 g (0.044 mmol) of **1-N_2H_4** and approximately 20 mL of heptane. On a high-vacuum line, the vessel was submerged in liquid nitrogen and evacuated. The contents of the vessel were heated to 110 °C overnight, yielding an orange solution. The remaining H_2 and the solvent were removed in vacuo, and the remaining solid was recrystallized from pentane at −35 °C to yield 0.018 g (47%) of a beige powder identified as **3**. Anal. Calcd for $C_{36}H_{52}Hf_2N_2$: C, 49.71; H, 6.03; N, 3.22. Found: C, 49.36; H, 5.71; N, 2.74. ^1H NMR (benzene-d_6, 23 °C): δ 0.97 (d, 10 Hz, 2H, Hf−$C\mathit{H}_2$), 1.18 (s, 6H, $C_5\mathit{Me}_4H$), 1.41 (d, 10 Hz, 2H, Hf−$C\mathit{H}_2$), 1.43 (s, 2H, N−*H*), 1.68 (s, 6H, $C_5\mathit{Me}_4H$), 1.75 (s, 6H, $C_5\mathit{Me}_4H$), 1.80 (s, 6H, $C_5\mathit{Me}_4H$), 1.84 (s, 6H, $C_5\mathit{Me}_4H$), 1.85 (s, 6H, $C_5\mathit{Me}_4H$), 1.99 (s, 6H, $C_5\mathit{Me}_4H$), 5.01 (s, 2H, $C_5Me_4\mathit{H}$), 5.87 (s, 2H, $C_5Me_4\mathit{H}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 11.14, 12.27, 12.53, 12.58, 12.85, 13.29, 13.86 ($C_5\mathit{Me}_4H$), 28.91 (Hf−$\mathit{C}H_2$), 102.56, 105.48, 108.43, 109.01, 112.44, 115.41, 117.81, 118.75, 119.03, 122.68 (C_5Me_4H). $^{15}N\{^1H\}$ NMR (toluene-d_8, 23 °C): δ 94.70. IR (benzene): ν_{N-H} 3307 cm^{-1}.

Spectroscopic Identification of (η^5-C_5Me_4H)$_2$Hf(CO)$_2$ (1-(CO$_2$)). A thick-walled reaction vessel was charged with 0.100 g (0.203 mmol) of **1-Cl_2**, 2.0 g (82.3 mmol) of magnesium powder, and approximately 20 mL of tetrahydrofuran. On a high-vacuum line, the vessel was submerged in liquid nitrogen and 1 atm of carbon monoxide was admitted. The contents of the vessel were warmed to 60 °C, and the resulting reaction mixture was stirred overnight, producing a colorless solution. The excess CO and solvent were removed in vacuo, the vessel was transferred into the drybox, and the remaining white residue was extracted with pentane and filtered through Celite. The pentane was removed, and the 0.021 mg (21%) of white powder was analyzed without further purification. ^1H NMR (benzene-d_6, 23 °C): δ 1.74 (s, 12H, $C_5\mathit{Me}_4H$), 2.08 (s, 12H, $C_5\mathit{Me}_4H$), 4.09 (s, 2H, $C_5Me_4\mathit{H}$). IR (pentane): ν_{C-O} 1945, 1849 cm^{-1}.

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Supporting Information Available: Crystallographic data for **1-N_2** and **1-N_2H_4**, including bond distances and angles, kinetic data for the hydrogenation(deuteration) of **1-N_2**, a sample ^1H NMR spectrum of **2**, and DFT calculations for **1-N_2**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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