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Addition of Methyl Triflate to a Hafnocene Dinitrogen Complex: Stepwise N_2 Methylation and Conversion to a Hafnocene Hydrazonato Compound

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Abstract: Treatment of the hafnocene complex bearing a strongly activated, side-on bound dinitrogen ligand, $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, with two equivalents of methyl triflate yielded a mixture of products, one of which was identified as the triflato hafnocene methyl diazenide compound, $(\eta^5\text{-}C_5Me_4H)_2Hf(OTf)(N_2(CH_3))$, arising from methylation of one of the nitrogen atoms. This reactivity contrasts with that of the zirconocene congener, $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, where methyl triflate addition yields a variety of products that lack new nitrogen−carbon bonds. The methylated hafnocene product, $(\eta^5\text{-}C_5Me_4H)_2Hf(OTf)(N_2(CH_3))$ provides a platform for additional transformations for the functionalized dinitrogen core. Treatment with additional methyl triflate results in a second nitrogen−carbon bond formation to yield a rare example of a triflato hafnocene hydrazonato complex. Loss of methane and formation of the hafnocene bis(triflate) accompany the transformation. Isotopic labeling studies and other experiments are consistent with a pathway involving initial methylation of the unsubstituted nitrogen in the methyl diazenido ligand followed by deprotonation by a triflate anion.

Introduction

The direct conversion of molecular nitrogen (N_2) to more complex nitrogen-containing compounds is a long-standing challenge in chemical synthesis.[1] Industrial ammonia synthesis, whereby N_2 is hydrogenated at high temperature and pressure over an activated iron−ruthenium catalyst, represents one of the most significant scientific and technological breakthroughs of the past century.[2−4] Synthetic NH_3 serves as the conduit to most nitrogen-containing molecules which have diverse applications including fertilizers, fuels, fine chemicals, pharmaceuticals, dyes, semiconductors and liquid crystal displays.[5] The high-energy costs and fossil fuel consumption associated with the venerable Haber−Bosch process inspire the search for direct, ammonia-independent pathways from atmospheric N_2 to important nitrogen-containing molecules. Key to realizing this goal is the discovery of new fundamental chemistry for formation of nitrogen−carbon bonds using N_2 as the nitrogen atom source.[6]

Over the past decade, the synthesis of strongly activated zirconium and hafnium dinitrogen compounds has opened new routes to nitrogen-element bond formation.[7,8] Methods for the assembly of N−H bonds are perhaps the most well developed, and functionalization reactions with dihydrogen[9−12] and C−H bonds,[11,13] and protonation by weak Brønsted acids including water[12,14,15] have been discovered. For nonpolar reagents, both experimental[13,16] and computational studies[16−19] support 1,2-addition of the E−H (E = H, hydrocarbyl) bonds to the M═N core through a highly ordered, four-centered transition structure, reminiscent of the chemistry known for zirconium imido

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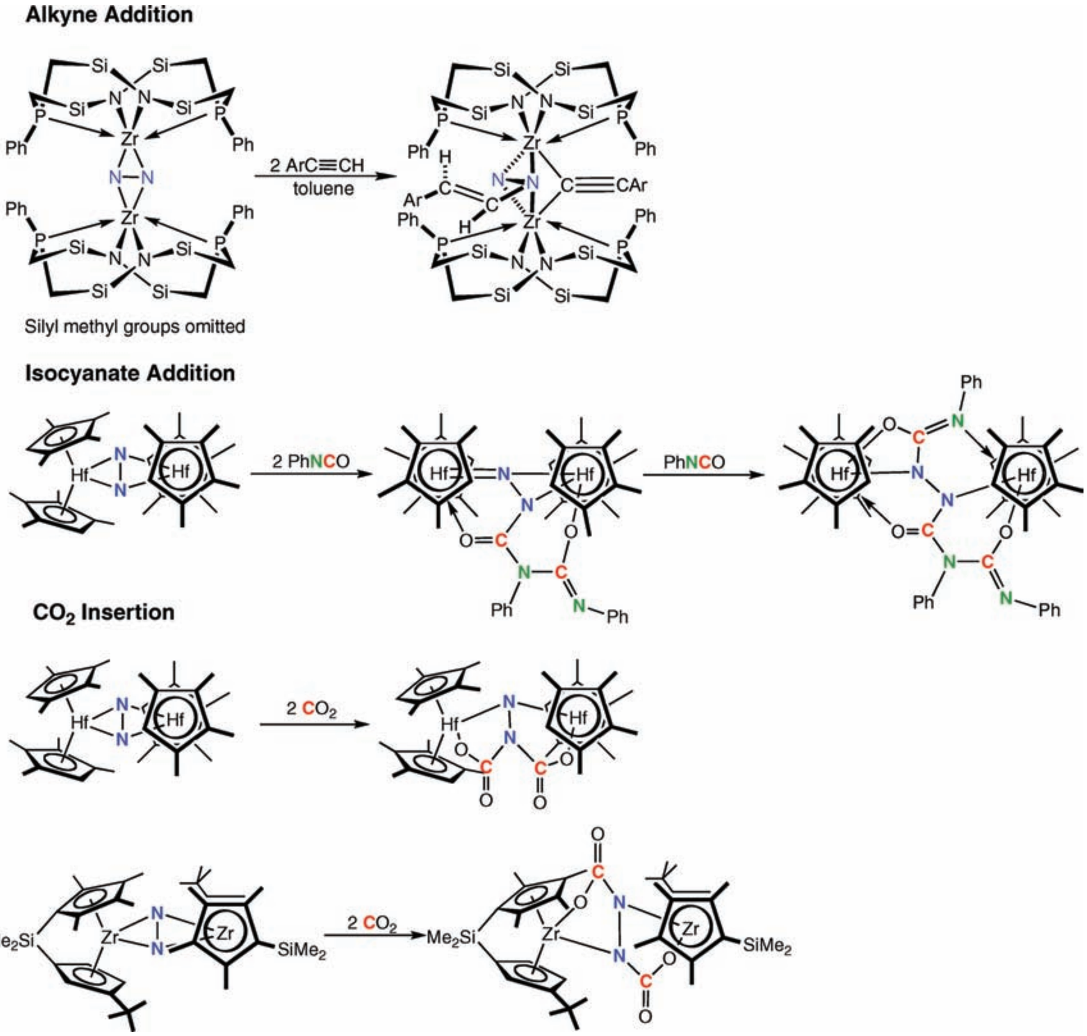
10.1021/ja904436a CCC: $40.75

Scheme 1



complexes.[20] This mechanistic paradigm offers a unique method for the functionalization of dinitrogen with nonpolar reagents.

With various routes to N−H bonds established, we and others have turned our attention to developing methods for nitrogen−carbon bond formation. As with N−H bond formation, cycloaddition routes akin to group 4 transition metal imido chemistry, are useful for N_2 functionalization with essentially nonpolar carbon sources (Scheme 1). Fryzuk and co-workers reported dinitrogen functionalization with terminal alkynes by initial [2 + 2] cycloaddition followed by cleavage of the Zr−C bond and protonation by a second equivalent of the acetylene.[21] Our laboratory reported the cycloaddition of isocyanates to the hafnocene dinitrogen complex, $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Hf}]_2(\mu_2,\eta^2,\eta^2\text{-N}_2)$, a reaction that induces unproductive N_2 loss from the zirconocene congener.[22] Both $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Hf}]_2(\mu_2,\eta^2,\eta^2\text{-N}_2)$[23] and the *ansa*-zirconocene dinitrogen complex, $[(\text{DOp})\text{Zr}]_2(\mu_2,\eta^2,\eta^2\text{-N}_2)$ (Dop = $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_5\text{H}_3\text{-3-}^t\text{Bu})$),[24] insert carbon dioxide into the metal−nitrogen bonds which leads to various dicarboxylated hydrazines following treatment with the appropriate electrophile.

Historically, nitrogen−carbon bond formation from coordinated N_2 has been accomplished by treatment of isolable group 6 transition metal dinitrogen complexes with electrophiles, most typically alkyl and acyl halides, or by protonation−condensation sequences with aldehydes and ketones.[25] This approach often results in functionalization of one of the two nitrogen atoms. In group 4 transition metal chemistry, elaboration of coordinated dinitrogen with various electrophiles dates to van Tamelen's seminal syntheses of amines and nitriles using ill-defined titanocene dinitrogen complexes.[26] Mori and co-workers have since expanded this approach and used mixtures of TiX_4 (X = halide, alkoxide), Li, and Me_3SiCl to incorporate molecular nitrogen into complex molecules such as pumiliotoxin C and lycopodine.[27]

Despite these advances, little is known about the reactivity of well-defined zirconocene and hafnocene complexes bearing

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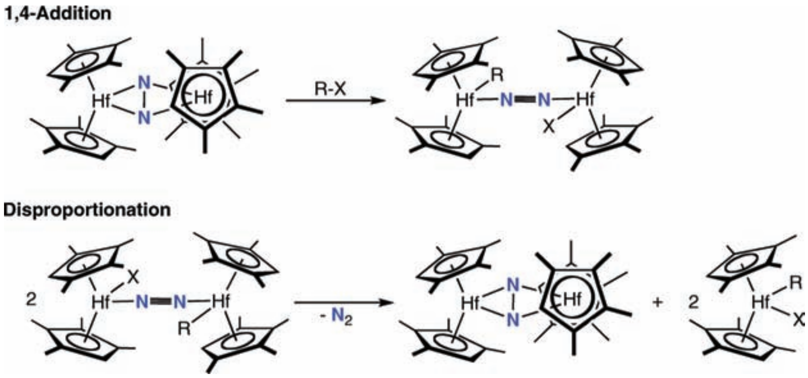
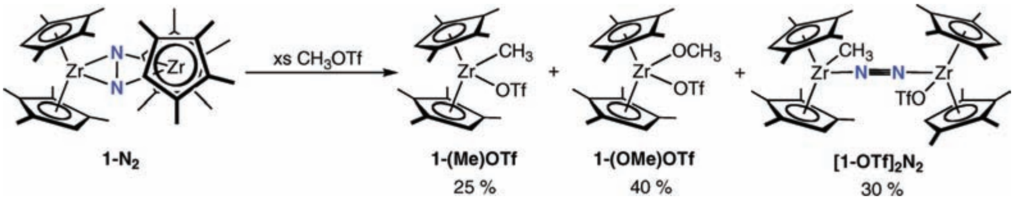
Scheme 2



Scheme 3



strongly activated dinitrogen ligands such as $[(\eta^5\text{-}C_5Me_4H)_2M]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (M = Zr, **1-N₂**; Hf, **2-N₂**) toward carbon-based electrophiles. In N−H bond-forming chemistry, zirconocene complexes with strongly activated N_2 ligands undergo protonation by H_2O to yield hydrazine in contrast to the weakly activated compound, $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, where hydrolysis results in N_2 dissociation.[28] Recent attempts to extend this chemistry to N−C bond formation by addition of alkyl halide electrophiles to $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ instead resulted in isolation of alkyl halide hafnocene dinitrogen complexes with weakly activated end-on dinitrogen ligands (Scheme 2).[29] Over time, these compounds undergo formal disproportionation with loss of N_2 to regenerate the starting side-on bound hafnocene dinitrogen complex and the hafnocene alkyl halide derivative (Scheme 2). The rate of the disproportionation reaction is dependent on both the identity of the halide and the alkyl substituent where smaller halides and alkyls promote faster reactions, a trend that is likely a result of the accessibility of the side-on dinitrogen haptomer.[29]

Sita and co-workers have recently reported a rare example of N_2 alkylation with a group 4 transition metal dinitrogen complex.[30] Addition of ethyl bromide to a cyclopentadienyl amidinate hafnium dinitrogen complex resulted in N−C bond formation. In this contribution, we describe a unique, stepwise N−C bond-forming sequence upon addition of methyl triflate to **2-N₂**. The first methylation event forms a hafnocene methyl diazenido complex while the second results in a rare hafnocene hydrazonato compound. The mechanism of the second N−C bond-forming reaction has been investigated with a series of isotopic labeling studies, concentration effects as well as with model reactions.

Results and Discussion

Attempted Dinitrogen Methylation with Side-on Bound Dinitrogen Compounds. Because previous studies from our laboratory established that alkyl halides do not promote nitrogen−carbon bond formation upon addition to either $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**1-N₂**) or $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**2-N₂**), other electrophiles, specifically methylating agents, were explored. Addition of methyl triflate to a benzene-d_6 solution of **1-N₂** produced a mixture of products (Scheme 3). Two, the zirconocene methyl triflate, **1-(Me)OTf** (25%), and the methoxy triflate, **1-(OMe)OTf** (40%), are derived from loss of N_2. In addition, a blue precipitate, identified as the end-on zirconocene dinitrogen compound, $[(\eta^5\text{-}C_5Me_4H)_2Zr(OTf)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, was isolated in approximately 30% yield. A small amount (<5%) of other unidentified zirconocene products were also formed.

Methyl triflate addition was also explored with the hafnocene dinitrogen complex, **2-N₂**, with the hope that the more activated N_2 compound would favor N−C bond formation over competing 1,4-addition or dinitrogen dissociation chemistry. Addition of a slight excess (2.2 equiv) of CH_3OTf to a benzene-d_6 solution of **2-N₂** resulted in a mixture of products arising from three distinct pathways (Scheme 4). The desired pathway, accounting for 35% of the mixture based on consumption of **2-N₂**, resulted in dinitrogen methylation and yielded the hafnocene triflato diazenide compound, **3**, along with an equimolar quantity of **2-(Me)OTf** byproduct. The second pathway furnished the major product, $[(\eta^5\text{-}C_5Me_4H)_2Hf(OTf)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (**[2-OTf]₂N₂**) along with ethane and was isolated in 60% yield. The final product, formed in 5% based on conversion of **2-N₂**, was identified as **2-(OMe)OTf** and arises from loss of dinitrogen. The characterization of each of these compounds arising from methyl triflate addition and likely pathways for their formation will be discussed below. Attempts to improve the yield of the N_2 methylation product by using $[Me_3O][BF_4]$ resulted in only N_2 loss and formation of the hafnocene difluoride, $(\eta^5\text{-}C_5Me_4H)_2HfF_2$.

As with the zirconium congener, the end-on triflato hafnocene dinitrogen complex, $[(\eta^5\text{-}C_5Me_4H)_2Hf(OTf)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$,

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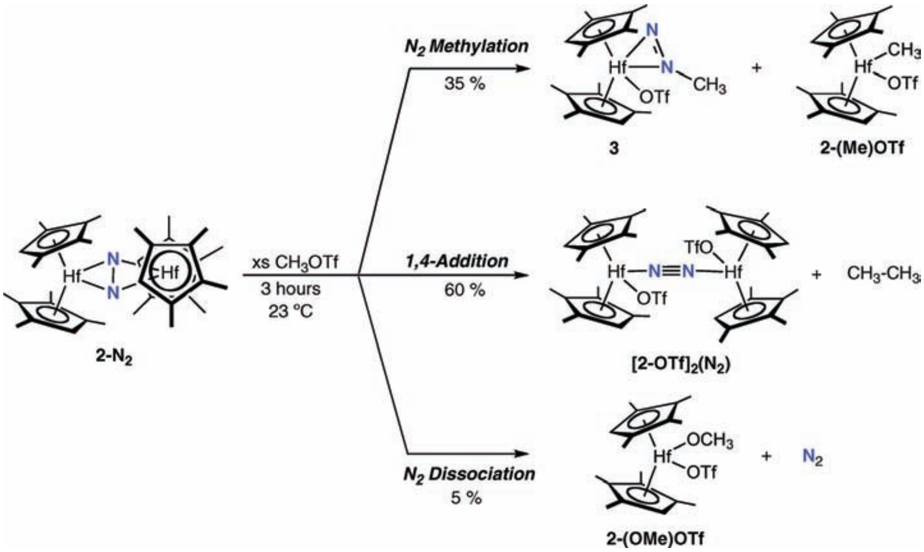
Scheme 4



[2-OTf]$_2$N$_2$, was sparingly soluble in benzene and therefore readily isolated as purple crystals. This compound likely forms from the 1,4-addition of methyl triflate to **2-N$_2$** to initially form [(η^5-C$_5$Me$_4$H)$_2$Hf(OTf)][(η^5-C$_5$Me$_4$H)$_2$Hf(CH$_3$)](μ_2,η^1,η^1-N$_2$), which undergoes subsequent reaction with additional methyl triflate to yield **[2-OTf]$_2$N$_2$**. Ethane was observed by ^{1}H NMR spectroscopy as a volatile byproduct. The solid-state structure of **[2-OTf]$_2$N$_2$** is presented in Figure 1 and confirms the end-on hapticity of the N$_2$ ligand. The dinitrogen ligand is weakly activated with N≡N and Hf−N bond distances of 1.189(8) and 2.060(4) Å, respectively.

The identification of **1-(OMe)OTf** and **2-(OMe)OTf**, albeit in relatively small quantities in the hafnocene case, from addition of methyl triflate to **1-N$_2$** and **2-N$_2$**, respectively, seems to violate the law of mass action. What is the origin of the additional oxygen atom? Several independent syntheses of hafnocene complexes were undertaken to answer this question and to confirm the identity of the other side products. Addition of one equivalent of silver triflate to (η^5-C$_5$Me$_4$H)$_2$HfMe$_2$ (**2-Me$_2$**) in toluene followed by filtration cleanly furnished (η^5-C$_5$Me$_4$H)$_2$Hf(Me)OTf (**2-(Me)OTf**), establishing its identity as one of the products from methyl triflate addition to **2-N$_2$**. Synthesis of **2-(OMe)OTf** was accomplished by treatment of a benzene-d_6 solution of **2-(Me)OTf** with a slight excess of methanol, thereby confirming its formation as a byproduct during dinitrogen methylation.

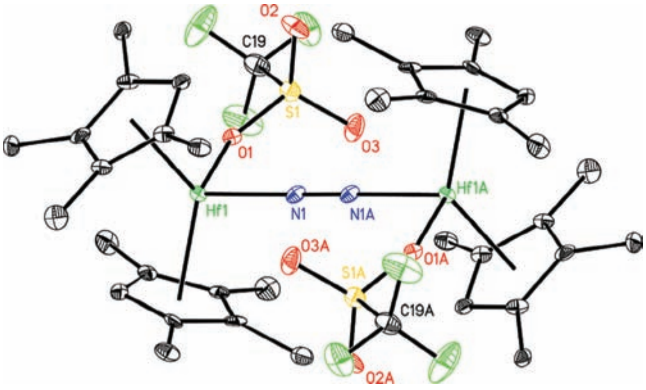
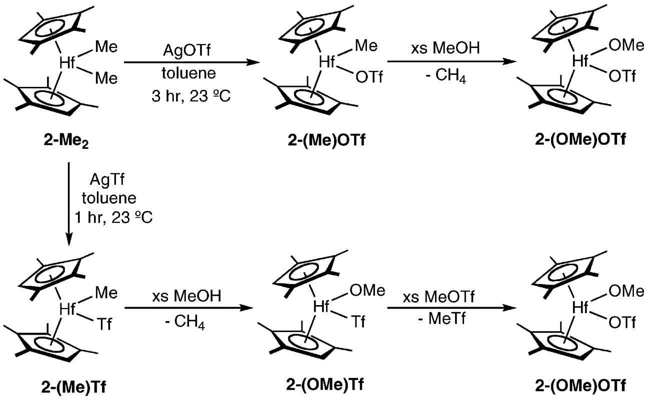


Figure 1. Molecular structure **[2-OTf]$_2$N$_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Possible origins of **2-(OMe)OTf** were also studied. It seems plausible that a hafnocene methoxy sulfone complex, (η^5-C$_5$Me$_4$H)$_2$Hf(OMe)Tf (Tf = −OS(O)CF$_3$) (**2-(OMe)Tf**), could arise from S−O bond cleavage and oxidative addition to "hafnocene". An independent synthesis of **2-(OMe)Tf** was pursued and was inspired by the successful synthesis of **2-(OMe)OTf** (Scheme 5). Treatment of **2-Me$_2$** with one equivalent of silver trifluoromethylsulfone yielded the desired hafnocene methyl sulfone complex, **2-(Me)Tf**. Subsequent addition of methanol resulted in liberation of methane and formation of the hafnocene methoxy sulfone, **2-(OMe)Tf**. This compound has distinct ^{1}H, ^{13}C and ^{19}F spectroscopic features from **2-(OMe)OTf** further substantiating its absence as a byproduct of methyl triflate addition to **2-N$_2$**. Importantly, addition of excess methyl triflate to a benzene-d_6 solution of **2-(OMe)Tf** resulted in rapid and quantitative conversion to **2-(OMe)OTf**. In the observed reaction chemistry, the competing pathways result in a continual excess of methyl triflate being present, meaning that if **2-(Me)Tf** is initially formed, it is likely rapidly converted to **2-(OMe)OTf** and is therefore not observed.

Compound **3** was of primary interest due to the presence of a functionalized dinitrogen ligand. Attempts to obtain the compound alone and in pure form by carrying the reaction out on relatively large scale followed by recrystallization furnished only mixtures. Various combinations of isotopologues (^{13}C, CD$_3$ and ^{15}N) were prepared and studied by multinuclear and

Scheme 5



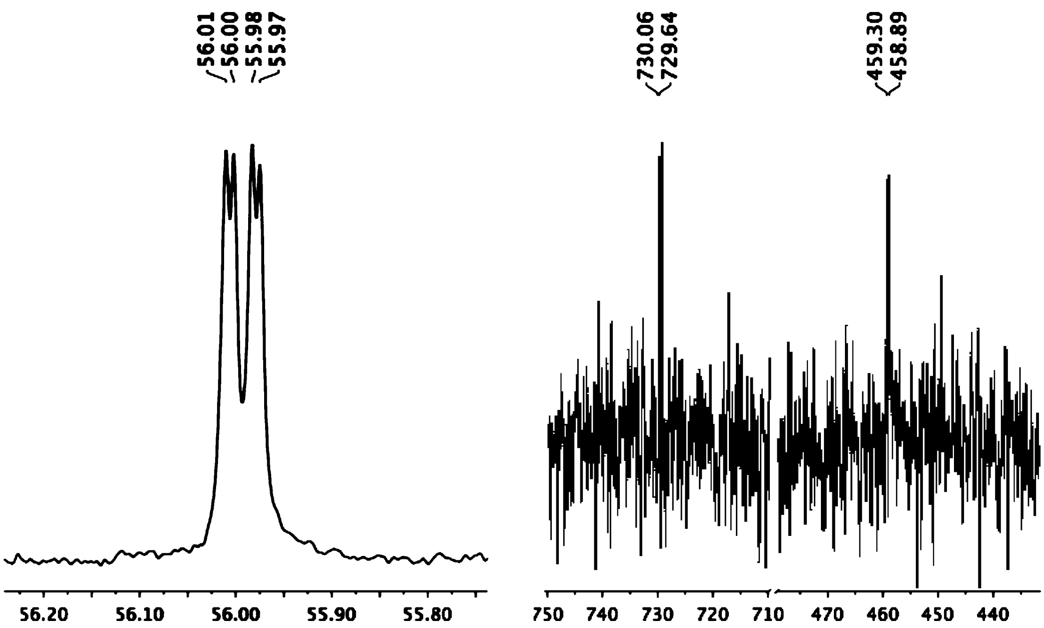


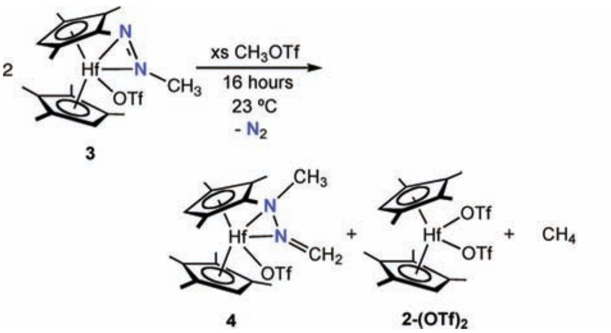
Figure 2. Partial benzene-d_6 $\{^1H\}^{13}C$ NMR spectrum of **3-^{13}C/^{15}N** (left) and ^{15}N NMR spectrum of **3-^{15}N** (right).

multidimensional NMR studies to establish nitrogen−carbon formation and the identity of the compound. These variants were accessed using the identical chemistry presented in Scheme 4 with readily available $^{13}CH_3OTf$, CD_3OTf, and $^{15}N_2$ gas.

The benzene-d_6 $\{^1H\}^{13}C$ NMR spectrum of the $^{13}C,^{15}N$ isotopologue (Figure 2) of **3** (denoted **3-^{13}C/^{15}N**) exhibited a doublet of doublets centered at 55.85 ppm and yielded coupling constants of $^1J_{N-C} = 3.5$ and $^2J_{N-C} = 1.1$ Hz. The ^{15}N NMR spectrum of ^{15}N isotopologue, **3-^{15}N**, exhibited two doublets centered at 460.1 and 729.8 ppm with a coupling constant of $^1J_{N-N} = 20.6$ Hz, establishing inequivalent nitrogens. On the basis of these data, the structure of **3** was established as the triflato hafnocene diazenide compound, $(\eta^5\text{-}C_5Me_4H)_2Hf(OTf)(N_2CH_3)$. On the basis of electron counting and literature precedent from a recently synthesized zirconium compound by Gade and co-workers,[31] we tentatively assign the η^2-haptomer as the ground state. The η^1 variant cannot be ruled out on the basis of the NMR data.[32] We note that no strong IR bands assignable to an N−N stretch have been observed, also supporting the η^2 assignment.

As mentioned previously, Gade and co-workers[31] have recently reported the synthesis of zirconium diazenido complexes from thermal decomposition of the corresponding hydrazinediide compounds. In analogy to **3**, both the 1-adamantyl- and mesityl-substituted diazenide ligands exhibit significantly downfield-shifted ^{15}N NMR resonances (804.2 ppm, R = ^{1}Ad; 810.9 ppm, R = Mes) for the unsubstituted nitrogen atom. DFT calculations also confirmed the assignment of the downfield ^{15}N peaks to the unsubstituted nitrogen atoms. These similar spectroscopic features also support the proposed η^2-hapticity for the methyl diazenido ligand in **3**.

The reactivity of **3** with additional methyl triflate was also studied in an attempt to promote a second nitrogen−carbon bond-forming reaction. Addition of excess (∼1 equiv based on the original amount of **2-N$_2$**) CH_3OTf to a benzene-d_6 solution of **3** at 23 °C yielded a new hafnocene product, **4**, along with methane gas and the hafnocene bis(triflate), **2-(OTf)$_2$** (eq 1). Complete consumption of **3** required approximately 16−18 h under these conditions, explaining why **4** was not observed initially. The yield of **4** is approximately 50% as judged by ^1H NMR spectroscopy. As will be presented during the mechanistic discussion, an equivalent of **3** is sacrificed in the formation of methane and **2-(OTf)$_2$**, rendering the normalized yield of **4** >95%.



(1)

The benzene-d_6 ^1H NMR spectrum of **4** exhibited singlets centered at 2.94 and 5.40 ppm, assigned to N−CH_3 and N=CH_2 groups, respectively. These assignments were confirmed by DEPT, HSQC, and HMBC NMR experiments as well as by preparation of the ^{13}C and ^2H isotopologues. Coupling constants of $^3J_{C-C} = 6.1$ Hz, $^1J_{C-N} = 2.3$ Hz, $^2J_{C-N} = 1.2$ Hz, and $^1J_{N-N} = 15.0$ Hz for the N−CH$_3$ signal were measured, and values of $^3J_{C-C} = 6.1$ Hz, $^1J_{C-N} = 11.5$ Hz, $^2J_{C-N} = 1.9$ Hz, and $^1J_{N-N} = 15.0$ Hz were determined for the N = CH$_2$ peak. The ^{15}N isotopologue was prepared from **3-^{15}N** and methyl triflate. Two doublets centered at 311.51 (N = CH$_2$) and 174.23 (N−CH$_3$) ppm were observed by ^{15}N NMR spectroscopy. On the basis of these data, the identity of **4** is assigned as the triflato hafnocene hydrazonato compound resulting from a second N−C bond-forming reaction with concomitant loss of methane and formation of **2-(OTf)$_2$**. As with **3**, the NMR data does not distinguish between η^2 and η^1 haptomers of the hydrazonato ligand. We

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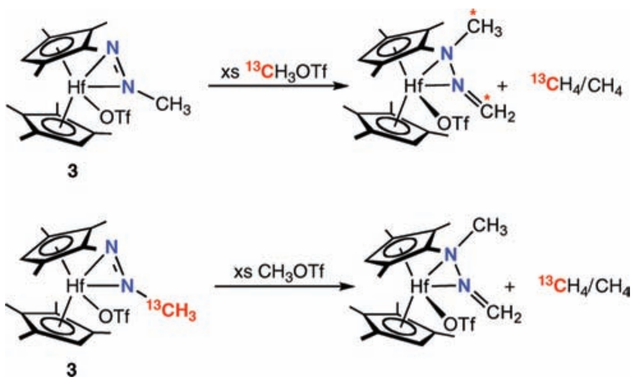
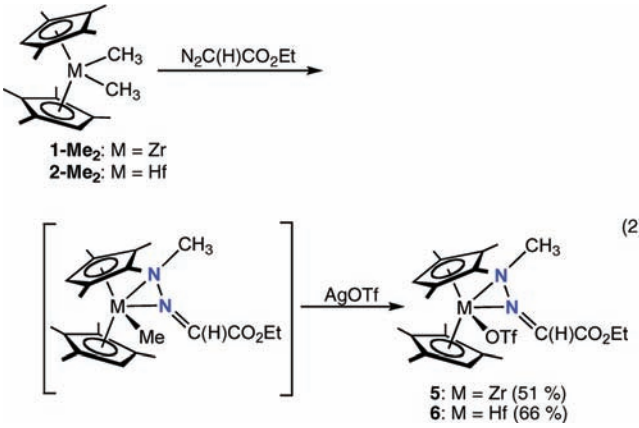
Scheme 6



tentatively favor the η^2 structure with the neutral donor occupying the central position in the hafnocene wedge, and all structures are drawn accordingly. Both the benzene solution and solid state (KBr) infrared spectra of **4** were recorded. However, no diagnostic bands assigned to the hydrazonato ligand could be identified.

Examples of zirconocene hydrazonato compounds have been previously synthesized by the insertion of diazoalkanes into Zr−C and Zr−H bonds[33] and mechanisms of their formation have been studied computationally.[34] To further explore the stability of this fragment and to prepare a hafnocene example, the independent syntheses of triflato zirconocene and hafnocene hydrazonato complexes were explored. Treatment of either **1-Me₂** or **2-Me₂** with commercially available ethyl diazoacetate followed by AgOTf addition furnished (η^5-$C_5Me_4H)_2Hf(OTf)$(η^2-$N(CH_3)N{=}C(H)COOEt$) (M = Zr, **5**; Hf, **6**) in moderate yields (eq 2). The ^1H and ^{13}C benzene-d_6 NMR spectra of **5** and **6** exhibit features similar to **4** (see the Experimental Section) supporting the evidence of the hafnocene hydrazonato complex from methyl triflate addition to **3**.



(2)

Isotopic labeling experiments were conducted to gain insight into the mechanism of conversion of **3** to **4**. Treatment of a benzene-d_6 solution of natural abundance **3** with $^{13}CH_3OTf$ resulted in incorporation of the isotopic label into *both* the methylene and methyl positions of **4** (Scheme 6). Analysis of the methane gas byproduct by ^1H NMR spectroscopy established formation of both $^{13}CH_4$ and CH_4 (Figure S8, Supporting Information). The converse experiment, addition of CH_3OTf to the ^{13}C isotopologue of **3**, also yielded a mixture of CH_4 and $^{13}CH_4$. In all of the ^{13}C-labeling experiments conducted in this work, no isotopic incorporation was observed in any of the side products formed from the synthesis of **3**. Importantly, the predominant methane isotopologue formed during the conversion of **3** to **4** is from the second equivalent of added methyl triflate and increases with the number of equivalents of MeOTf added.

The reversibility of the second carbon−nitrogen bond-forming step was also probed with ^{13}C and ^2H labeling studies. Addition of $^{13}CH_3OTf$ to a solution of **3** and monitoring the reaction mixture by ^{13}C NMR spectroscopy revealed growth of the N−$^{13}CH_3$ peak centered at 55.85 ppm in **3** over the course of 3 h at 23 °C *prior* to conversion to **4**. The converse experiment, addition of natural abundance CH_3OTf to **3-^{13}C** placed natural abundance methyl groups in **4** along with both isotopologues of methane (see Supporting Information (SI)). Similar results were obtained from deuterium labeling. Treatment of **3-d_3**, prepared from addition of CD_3OTf to **2-N₂**, with CH_3OTf resulted in growth of the N−CH_3 peak centered at 4.11 ppm in the ^1H NMR spectrum of **3** *prior* to conversion to **4**. Both experiments clearly establish fast and reversible nitrogen methylation prior to formation of the triflato hafnocene hydrazonato compound, **4**.

In addition to being a convenient probe for the reversibility of nitrogen methylation, deuterium-labeling studies also provided additional insight into the mechanism of methane formation and whether methyl groups remain intact as $[CH_3]/[CD_3]$ units or are isotopically modified during the conversion of **3** to **4**. Treatment of **3-d_3** (as a mixture with **2-(CD₃)OTf**) with CH_3OTf yielded **4-d_n** along with CH_4 and CH_3D as the principal isotopologues of methane as judged by ^1H NMR spectroscopy (Figure S8, SI). It is possible that CD_3H was formed at low concentration but was not detected by ^1H NMR spectroscopy. Analysis of **4-d_n** by ^1H NMR spectroscopy established hydrogen incorporation into both the $N{-}CD_3$ and $N{=}CD_2$ positions, consistent with methyl group exchange in **3**.

The converse isotopic labeling experiment, addition of CD_3OTf to natural abundance **3**, was also conducted (Scheme 7). As expected, deuterium incorporation was observed in the $N{-}CH_3$ and $N{=}CH_2$ positions as judged by ^2H NMR spectroscopy. To definitively characterize the isotopologues of methane produced, gas-phase infrared experiments were conducted. This technique is more sensitive than ^1H NMR spectroscopy for identifying methane isotopologues including CD_4. After the addition of CD_3OTf to **3**, the reaction was stirred overnight, and the volatile components were then removed and collected with a Toepler pump. The methane was collected in a gas-phase IR cell and analyzed. As shown in Figure 3, bands for CH_4, CD_4, CH_3D (trace), and CD_3H are observed. Importantly, there is no evidence for formation of CH_2D_2.

Because **2-(Me)OTf** was a byproduct from the synthesis of **3** and was not separated for subsequent studies, control experiments were conducted to establish the behavior of this compound toward various isotopologues of methyl triflate. Addition of methyl triflate to a benzene-d_6 solution of **2-(Me)OTf** produced no reaction over the course of days at 23 °C. Likewise, treatment of **2-(Me)OTf** with excess $^{13}CH_3OTf$ did not result in exchange of the isotopic label into the hafnium

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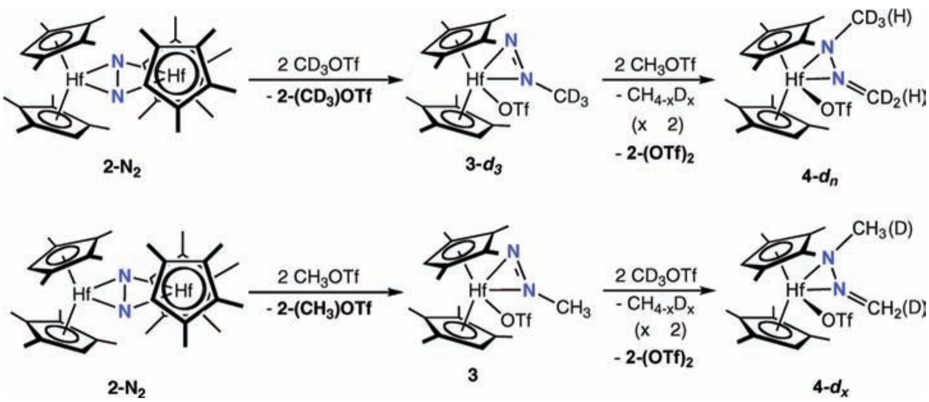
(33) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 2029. (b) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994. (c) Bai, G.; Roesky, H. W.; Hao, H.; Noltenmeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2001**, *40*, 2424.

(34) Hay, J. P. *Organometallics* **2007**, *26*, 4424.

(35) Wilmshurst, J. K; Bernstein, H. J. *Can. J. Chem.* **1957**, *35*, 226.

Scheme 7



compound. By contrast, addition of one equivalent of HOTf to a benzene-d_6 solution of **2-(Me)OTf** resulted in immediate formation of **2-(OTf)$_2$** with concomitant formation of methane. The results of all of these experiments also demonstrate that the methyl triflate used is not detectably contaminated with HOTf.

Crossover experiments were also conducted. Mixing benzene solutions of the ^{13}C isotopologue of **4**, **4-^{13}C$_2$**, with a benzene-d_6 solution of **3-*d*$_3$** produced no change over the course of days at 23 °C as judged by ^{13}C NMR spectroscopy. No ^{13}C enrichment was observed in **3-*d*$_3$** or ^{2}H incorporation into **4-^{13}C$_2$**. Therefore, there is no exchange between the starting materials and products. One additional crossover experiment was conducted to evaluate the possibility of hafnocene methyl group exchange. A benzene-d_6 solution of **3-^{13}C** was prepared and included the appropriate amount of **2-(^{13}CH$_3$)OTf**. To this was added **2-(CH$_3$)OTf** and ^{13}CH$_3$OTf. The formation of **4-^{13}C$_2$**was monitored by ^{1}H NMR spectroscopy and revealed no incorporation of natural abundance [CH$_3$] into the final product.

One final series of experiments was performed to evaluate the effect of the concentration of added methyl triflate on the conversion of **3** to **4**. Because of the number of side products present in solution, quantitative kinetic analyses could not be carried out. With one equivalent of added methyl triflate, the half-life for the conversion of **3** to **4** at 23 °C was 48 h. At 15 equiv of added MeOTf, the conversion was complete within 4 h, establishing a rate dependence on added methyl triflate. Representative NMR data from these experiments is presented in the SI.

On the basis of all of the experimental data, a mechanistic pathway to account for the conversion of **3** to **4** upon addition of methyl triflate is presented in Scheme 8. Added methyl triflate is denoted in red for accounting purposes and to highlight the results of the isotopic labeling experiments. The sequence begins with methylation of the unsubstituted nitrogen atom in **3** to form a cationic hafnium dimethyl diazene intermediate. The neutral diazene ligand is free to exchange the methyl positions from the lateral to central sites in the hafnocene wedge by either dissociation/recoordination or by rotation. The methylation of **3** with MeOTf must be both fast and reversible as both ^{13}C- and ^{2}H-labeling experiments demonstrate isotopic incorporation into the starting compound before conversion to **4**. To form **4**, deprotonation of one of the methyl groups of the dimethyl

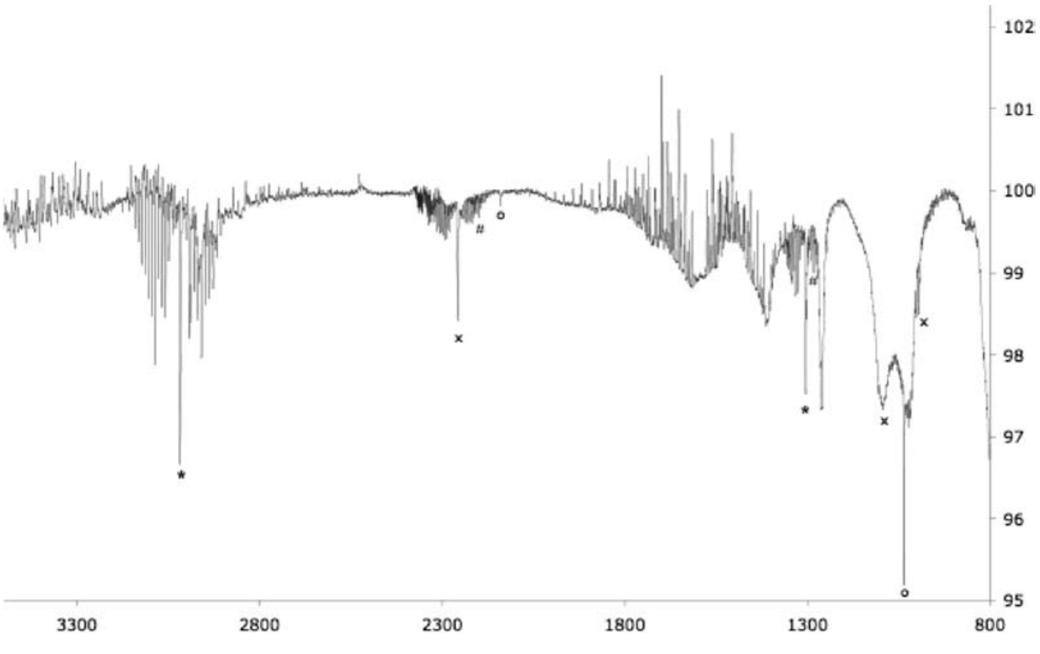
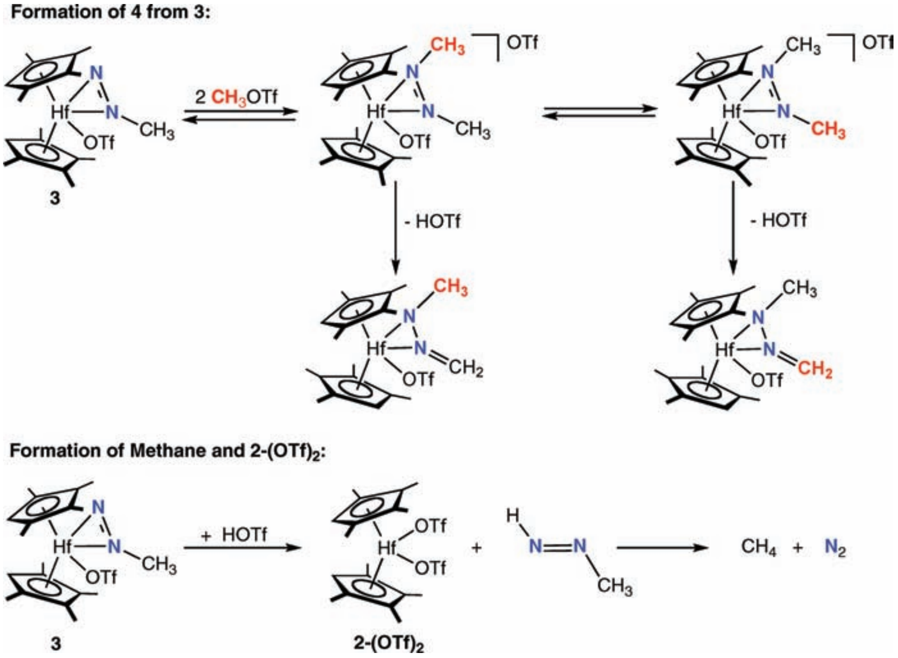


Figure 3. Gas-phase infrared spectrum of **3** with excess CD$_3$OTf establishing formation of CH$_4$ (*, 3019 and 1306 cm^{-1}), CD$_4$ (×, 2259, 1094, and 996 cm^{-1}), CH$_3$D (#, 2200 and 1300 cm^{-1}), and CD$_3$H (○, 2142 and 1036 cm^{-1}). Assignments are based on data reported in ref 35.

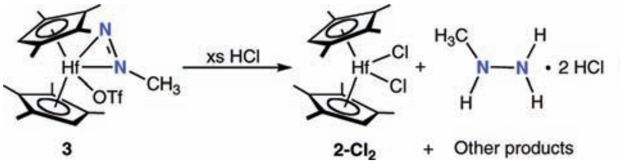
Scheme 8



diazene ligand by triflate takes place with concomitant release of HOTf. Distinguishing the site of deprotonation (either lateral or central position of the hafnocene wedge) is not possible on the basis of the available experimental data. It should be noted that the resulting hydrazonato complex can likely undergo η^2,η^1 interconversion to form the thermodynamically preferred isomer.

The mechanism proposed in Scheme 8 also accounts for the observation of the various methane isotopologues and formation of **2-(OTf)$_2$**. Recall that the predominant methane isotopologue observed is derived from the added methyl triflate. For example, treatment of **3** with excess $^{13}CH_3OTf$ yielded a majority of $^{13}CH_4$. In the proposed pathway, the formed HOTf could potentially react with the **2-(Me)OTf** present to form **2-(OTf)$_2$** and release methane. In this scenario, the predominant methane isotopologue formed would be from the original methylation as **2-(Me)OTf** is a byproduct from the synthesis of **3**. Also one would expect consumption of **2-(Me)OTf** during conversion to **4**, and this is not observed. A possibility more consistent with the data is that the in situ generated HOTf reacts more rapidly with remaining **3**. Because the methylation of **3** is fast and reversible, the second equivalent of added methyl triflate incorporates into **3** and is ultimately lost as methane. Also consistent with the mechanism proposed in Scheme 8, as the number of equivalents of the second methyl triflate addition is increased, the predominance of the isotopologue derived from that addition also increases. Thus, by adding more of a specific isotopologue of methyl triflate to **3**, more of that isotopologue is incorporated into the diazenido ligand and is ultimately released as methane.

To experimentally validate these hypotheses, a benzene-d_6 solution of **3** was treated with HOTf. Immediate formation of **2-(OTf)$_2$** and methane was observed. Trace amounts (<10%) of methylhydrazine were detected from this experiment. It is known that free methyldiazene, $CH_3N{=}NH$, undergoes decomposition to methane and N_2[36] and accounts for formation of CH_4 observed from the control experiment and the conversion of **3** to **4**. Treatment of a benzene-d_6 solution of **3** with a large excess (>10 equiv) of the mineral acid HCl yielded the hafnocene dichloride, **2-Cl$_2$**, along with free *N*-methylhydrazine as its HCl salt (eq 3). The hydrazine derivative was characterized by comparison of the D_2O solution ^1H and $\{^1H\}^{13}C$ NMR spectra to an authentic sample obtained commercially. Other minor products accompany the protonation products, and the fate of the triflate from these experiments is unknown.



(3)

An alternative mechanism was also considered and is presented in Figure S9 of the SI. This pathway involves initial reversible β-hydrogen elimination from **3** to form **2-(H)OTf** and diazomethane. The added methyl triflate serves to convert **2-(H)OTf** to **2-(OTf)$_2$**, allowing the diazomethane to insert into the hafnium methyl bond of **2-(Me)OTf** to yield **4**. However, the absence of crossover in the experiment whereby the conversion of **3-^{13}C** with $^{13}CH_3OTf$ was conducted in the presence of natural abundance **3-(Me)OTf** eliminates this mechanistic pathway. Additionally β-hydrogen elimination from coordinatively saturated **3** also seems unlikely.

Concluding Remarks

A rare example of stepwise formation of nitrogen–carbon bonds to coordinated dinitrogen has been observed with a hafnocene complex bearing a strongly activated, side-on bound N_2 ligand. The success of the N_2 functionalization reaction is specific to the electrophile and the metal dinitrogen complex; N–C bond formation is only observed upon addition of methyl triflate to the hafnocene congener. Even when dinitrogen methylation occurs, 1,4-addition of the electrophile to yield an end-on hafnocene dinitrogen compound remains competitive. The first addition of methyl triflate yields a rare example of a

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[36] (a) Tsuji, T.; Kosower, E. M. *J. Am. Chem. Soc.* **1970**, *92*, 1429. (b) Ackermann, M. N.; Ellenson, J. L.; Robison, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 7173.

triflato hafnocene methyl diazenido compound. Addition of excess methyl triflate forms a triflato hafnocene hydrazonato compound along with methane and the hafnocene bis(triflate). Isotopic labeling studies and other experiments establish that the second methyl triflate addition proceeds via reversible methylation of the unsubstituted nitrogen atom followed by deprotonation by triflate.

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.[37] Toluene, benzene, pentane, and heptane were further dried by distillation from "titanocene".[38] Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. The zirconocene and hafnocene dinitrogen complexes, **1-N$_2$** and **2-N$_2$**, were prepared according to literature procedures.[10,39] **2-^{15}N$_2$** was prepared by reduction of **2-I$_2$** under an atmosphere of ^{15}N$_2$.[11] AgTf[40] and **2-Me$_2$**[11] were also prepared according to literature procedures.

^{1}H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts were reported relative to SiMe$_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. ^{2}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 76.848, 125.716, and 50.663 MHz, respectively. ^{2}H and ^{13}C chemical shifts were reported relative to SiMe$_4$ using chemical shifts of the solvent as a secondary standard where applicable. ^{15}N chemical shifts were reported relative to liquid NH$_3$ using an external standard. ^{19}F NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 376.127 MHz and referenced to hexafluorobenzene.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer 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. Infrared spectroscopy was conducted on a Mattson RS-10500 Research Series FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Characterization data for [(η^5-C$_5$Me$_4$H)$_2$Zr(OTf)]$_2$(μ^2,η^1,η^1-N$_2$) ([1-OTf]$_2$N$_2$): Anal. Calcd for C$_{38}$H$_{52}$Zr$_2$N$_2$O$_6$S$_2$F$_6$: C, 45.95; H, 5.28; N, 2.82. Found: C, 46.09; H, 5.06; N, 2.64. IR (KBr) $\nu_{\mathrm{N-N}} = 1617$ cm^{-1}.

Preparation of (η^5-C$_5$Me$_4$H)$_2$ZrMe$_2$ (1-Me$_2$). A 20 mL scintillation vial was charged with 0.300 g (0.742 mmol) of (η^5-C$_5$Me$_4$H)$_2$ZrCl$_2$ (**1-Cl$_2$**) and approximately 10 mL of diethyl ether. The solution was chilled to −35 °C, and 1.16 mL (1.85 mmol) of a 1.6 M methyl lithium solution in diethyl ether was added via microsyringe. The reaction mixture was stirred at ambient temperature for 16 h, and the solvent was removed in vacuo. The resulting white residue was extracted with pentane and filtered to give 0.166 g (61%) of **1-Me$_2$** as a white solid. Anal. Calcd for C$_{20}$H$_{32}$Zr: C, 66.05; H, 8.87. Found: C, 66.01; H, 9.00. ^{1}H NMR (benzene-d_6, 23 °C): δ −0.54 (s, 6H, Hf−CH_3), 1.68 (s, 12H, C$_5$$Me_4$H), 1.94 (s, 12H, C$_5$$Me_4$H), 4.73 (s, 2H, C$_5$$Me_4$H). {^{1}H}^{13}C NMR (benzene-d_6, 23 °C): δ 121.79, 116.67, 110.53, 105.75 (Cp), 93.00 (C$_5$Me$_4$H), 35.32 (Hf−CH$_3$), 13.67, 11.98 (Cp).

Preparation of (η^5-C$_5$Me$_4$H)$_2$Zr(O$_3$SCF$_3$)Me (1-Me(OTf)). A 20 mL scintillation vial was charged with 0.080 g (0.220 mmol) of **1-Me$_2$**, 0.062 g (0.240 mmol) of AgOTf and approximately 5 mL of toluene. The reaction mixture was stirred at ambient temperature for 3 h the solvent removed in vacuo and the resulting dark residue extracted with pentane. Following filtration to remove Ag^0 precipitate, recrystallization at −35 °C afforded 0.046 g (42%) of **1-Me(OTf)** as a white powder. Anal. Calcd for C$_{20}$H$_{29}$F$_3$SO$_3$Zr: C, 48.26; H, 5.87. Found: C, 47.98; H, 6.02. ^{1}H NMR (benzene-d_6, 23 °C): δ 0.23 (s, 3H, Hf−CH_3), 1.40 (s, 6H, C$_5$$Me_4$H), 1.79 (s, 6H, C$_5$$Me_4$H), 1.82 (s, 6H, C$_5$$Me_4$H), 1.85 (s, 6H, C$_5$$Me_4$H), 5.05 (s, 2H, C$_5Me_4$$H$). {^{1}H}^{13}C NMR (benzene-d_6, 23 °C): δ 125.54, 125.08, 119.00, 117.86 (Cp), 108.50 (C$_5$Me$_4$H), 40.95 (Hf−CH$_3$), 11.57, 11.52. 9.93, 9.45 (Cp), CF$_3$ signal not located. ^{19}F NMR (benzene-d_6, 23 °C): δ −77.07.

Preparation of (η^5-C$_5$Me$_4$H)$_2$Zr(OMe)OTf ((1-OMe)OTf). A J. Young tube was charged with 0.012 g (0.024 mmol) of **1-(Me)OTf** and approximately 0.5 mL of benzene-d_6. On a high vacuum line, two equivalents of methanol were added via calibrated gas bulb (28 Torr in a 31.6 mL bulb). The colorless reaction mixture was transferred to a 20 mL scintillation vial after 1 h and dried, affording 0.012 g (94%) of **1-(OMe)OTf** as a white powder. Anal. Calcd. for C$_{20}$H$_{29}$F$_3$SO$_4$Zr: C, 46.76; H, 5.69. Found: C, 46.55; H, 5.48. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.67 (s, 6H, C$_5$$Me_4$H), 1.72 (s, 6H, C$_5$$Me_4$H), 1.78 (s, 6H, C$_5$$Me_4$H), 1.94 (s, 6H, C$_5$$Me_4$H), 3.90 (s, 3H, OC$H_3$), 5.57 (s, 2H, C$_5Me_4$$H$). {^{1}H} ^{13}C NMR (benzene-d_6, 23 °C): δ 113.15 (C$_5$Me$_4$H), 60.47 (Hf−OCH$_3$), 13.07, 11.24 (Cp), quaternary signals not located. ^{19}F NMR (benzene-d_6, 23 °C): δ −77.17.

Treatment of [(η^5-C$_5$Me$_4$H)$_2$Hf]$_2$(μ^2,η^1,η^1-N$_2$) with Methyl Triflate. A J. Young tube was charged with 0.010 g (0.011 mmol) of **2-N$_2$** and approximately 0.5 mL of benzene-d_6. On a high vacuum line, two equivalents of methyl triflate were added via calibrated gas bulb (32 Torr in a 13.1 mL bulb). Over the course of 1 h the solution turned from violet to deep pink to yellow with some dark-violet precipitate. The dark solid was identified as [(η^5-C$_5$Me$_4$H)$_2$Hf(OTf)]$_2$(μ^2,η^1,η^1-N$_2$) by X-ray diffraction and combustion analysis. Benzene-d_6 solution ^{1}H NMR spectroscopy of the soluble products revealed a 1:1 ratio of **2-(Me)OTf** and **3**. Three additional equivalents of methyl triflate were then added to the reaction mixture via calibrated gas bulb (18 Torr in a 31.6 mL bulb). Over the course of 16 h, the solution turned light yellow; analysis of the mixture by NMR spectroscopy revealed complete consumption of **3** along with the formation of **4** and **2-(OTf)$_2$** in a 1:1 ratio.

Characterization data for [(η^5-C$_5$Me$_4$H)$_2$Hf(OTf)]$_2$(N$_2$Me) (3: ^{1}H NMR (benzene-d_6, 23 °C): δ 1.24 (s, 12H, C$_5$$Me_4$H), 1.66 (s, 12H, C$_5$$Me_4$H), 1.83 (s, 12H, C$_5$$Me_4$H), 1.87 (s, 12H, C$_5$$Me_4$H), 4.11 (s, 6H, N−C$H_3$), 5.30 (s, 2H, C$_5Me_4$$H$). {^{1}H}^{13}C NMR (benzene-d_6, 23 °C): δ 10.51, 11.61, 12.06, 12.32 (C$_5$Me$_4$H), 55.85 (N−CH$_3$; ^{15}N−^{13}CH$_3$, dd, 5.1 Hz, 1.1 Hz), 109.96 (CpH), quaternary signals not located. ^{19}F NMR (benzene-d_6, 23 °C): δ −75.94. ^{15}N NMR (benzene-d_6, 23 °C): δ 460.13 (N-CH$_3$, d, $^1J_{\mathrm{NN}} = 20.6$ Hz), 729.86 (N=N(CH$_3$)).

Characterization data for [(η^5-C$_5$Me$_4$H)$_2$Hf(OTf)]$_2$(μ^2,η^1,η^1-N$_2$) ([2-OTf]$_2$(N$_2$)): Anal. Calcd for C$_{40}$H$_{52}$Hf$_2$N$_2$O$_6$S$_2$F$_6$: C, 39.08; H, 4.49; N, 2.40. Found: C, 39.10; H, 4.06; N, 2.81. IR (KBr) $\nu_{\mathrm{S-O}} = 1335$ cm^{-1}.

Preparation of (η^5-C$_5$Me$_4$H)$_2$Hf(O$_3$SCF$_3$)Me (2-(Me)OTf). A 20 mL scintillation vial was charged with 0.080 g (0.177 mmol) of **2-Me$_2$**, 0.055 g (0.195 mmol) of AgOTf and approximately 5 mL of toluene. The reaction mixture was stirred at ambient temperature for 3 h the solvent removed in vacuo and the resulting

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

(38) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

(39) Bernskoetter, W. H.; Olmos, A. V.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 1021.

(40) Hendrickson, J. S.; Skipper, P. L. *Tetrahedron* **1976**, *32*, 1627.

dark residue extracted with pentane. Following filtration to remove Ag^0 precipitate, recrystallization at −35 °C afforded 0.041 g (39%) of **2-Me(OTf)** as a white powder. Anal. Calcd for $C_{20}H_{29}HfO_3SF_3$: C, 50.36; H, 5.28. Found: C, 49.91; H, 5.10. ^{1}H NMR (benzene-*d*$_6$, 23 °C): δ 0.10 (s, 3H, Hf−C*H*$_3$), 1.49 (s, 6H, C$_5$Me$_4$*H*), 1.83 (s, 6H, C$_5$*Me*$_4$H), 1.84 (s, 6H, C$_5$*Me*$_4$H), 1.87 (s, 6H, C$_5$*Me*$_4$H), 5.10 (s, 2H, C$_5$Me$_4$*H*). {^{1}H} ^{13}C NMR (benzene-*d*$_6$, 23 °C): δ 12.08, 12.73, 14.24, 14.31 (C$_5$Me$_4$H), 42.04 (Hf−*C*H$_3$), 110.85, 119.01, 120.14, 126.64, 126.80 (Cp), CF$_3$ signal not located. ^{19}F NMR (benzene-*d*$_6$, 23 °C): δ −75.71.

Preparation of (η^5-C$_5$Me$_4$H)$_2$Hf(OMe)OTf ((2-OMe)OTf). A J. Young tube was charged with 0.015 g (0.026 mmol) of **2-(Me)OTf** and approximately 0.5 mL of benzene-*d*$_6$. On a high vacuum line, two equivalents of methanol were added via calibrated gas bulb (15 Torr in a 31.6 mL bulb). The colorless reaction mixture was transferred to a 20 mL scintillation vial after 1 h and dried, affording 0.014 g (95%) of **2-(OMe)OTf** as a white powder. Anal. Calcd. for $C_{20}H_{29}F_3SO_4Hf$: C, 39.97; H, 4.86. Found: C, 39.78; H, 4.80. ^{1}H NMR (benzene-*d*$_6$, 23 °C): δ 1.73 (s, 6H, C$_5$*Me*$_4$H), 1.77 (s, 6H, C$_5$*Me*$_4$H), 1.82 (s, 6H, C$_5$*Me*$_4$H), 1.99 (s, 6H, C$_5$*Me*$_4$H), 3.96 (s, 3H, OC*H*$_3$), 5.52 (s, 2H, C$_5$Me$_4$*H*). {^{1}H} ^{13}C NMR (benzene-*d*$_6$, 23 °C): δ 127.46, 126.74, 118.76, 117.09 (Cp), 112.02 (C$_5$Me$_4$H), 58.57 (Hf-*C*H$_3$), 13.05, 12.84. 11.21, 11.10 (Cp), CF$_3$ signal not located. ^{19}F NMR (benzene-*d*$_6$, 23 °C): δ −76.94.

Characterization Data for (η^5-C$_5$Me$_4$H)$_2$Hf(OTf)(η^2-N(CH$_3$)-*N*=CH$_2$) (4). ^{1}H NMR (benzene-*d*$_6$, 23 °C): δ 1.76 (s, 6H, C$_5$*Me*$_4$H), 1.84 (s, 6H, C$_5$*Me*$_4$H), 1.87 (s, 6H, C$_5$*Me*$_4$H), 1.89 (s, 6H, C$_5$*Me*$_4$H), 2.94 (s, 3H, N−C*H*$_3$), 5.40 (s, 2H, C*H*$_2$), 5.76 (s, 2H, C$_5$Me$_4$*H*). {^{1}H}^{13}C NMR (benzene-*d*$_6$, 23 °C): δ 10.77, 11.28, 11.44, 13.00 (C$_5$*Me*$_4$H), 33.13 (N-*C*H$_3$), 108.47 (*C*H$_2$), other signals not located. {^{1}H}^{15}N NMR (benzene-*d*$_6$, 23 °C): δ 174.23 (N−CH$_3$, d, $^1J_{NN}$ = 17.1 Hz), 311.49 (*N*=CH$_2$).

Procedure for the Liberation of *N*-Methylhydrazine·2 HCl. Approximately 10 mg of **3** (along with associated byproducts) was prepared by methyl triflate addition to **2-N$_2$** in benzene-*d*$_6$. The contents of the tube were frozen in liquid nitrogen, and approximately 10 equivalents of anhydrous HCl (vacuum transferred from a solution in dioxane) was added via calibrated gas volume. The solution was thawed and shaken, and the volatiles were removed in vacuo. The resulting solids were dissolved in D$_2$O, the ^{1}H and ^{13}C NMR spectra were recorded, and the desired product was confirmed by comparison to an authentic commercial sample.

Preparation of (η^5-C$_5$Me$_4$H)$_2$Hf(O$_3$SCF$_3$)$_2$ (2-OTf$_2$). A 20 mL scintillation vial was charged with 0.050 g (0.102 mmol) of **2-Cl$_2$**, 0.060 g (0.213 mmol) of AgOTf, and approximately 10 mL of toluene. The reaction mixture was stirred at ambient temperature for 8 h the solvent removed in vacuo and the resulting white residue extracted with diethyl ether. Following filtration to remove AgCl precipitate, recrystallization at −35 °C afforded 0.021 g (29%) of **2-(OTf)$_2$** as colorless crystals. Anal. Calcd for $C_{20}H_{26}HfO_6S_2F_6$: C, 33.41; H, 3.46. Found: C, 34.26; H, 3.65. ^{1}H NMR (benzene-*d*$_6$, 23 °C): δ 1.78 (s, 12H, C$_5$*Me*$_4$H), 1.89 (s, 12H, C$_5$*Me*$_4$H), 5.80 (s, 2H, C$_5$*Me*$_4$H). {^{1}H}^{13}C NMR (benzene-*d*$_6$, 23 °C): δ 11.57, 12.92 (C$_5$*Me*$_4$H), 116.42, 122.73, 131.91 (Cp), CF$_3$ signal not located. ^{19}F NMR (benzene-*d*$_6$, 23 °C): δ −75.00.

Preparation of (η^5-C$_5$Me$_4$H)$_2$Hf(OMe)(Tf) (2-(OMe)Tf). A 20 mL scintillation vial was charged with 2-Me$_2$ (30 mg, 0.067 mmol), AgSO$_2$CF$_3$ (16 mg, 0.067 mmol), and 5 mL of benzene. The reaction mixture was stirred at ambient temperature for 1 h the solvent removed in vacuo and the resulting dark residue extracted with pentane. Following filtration to remove the Ag° precipitate, the solvent was removed in vacuo, and the remaining solid was dissolved in benzene and transferred to a thick-walled bomb. On a high vacuum line, MeOH (40 Torr in a 100.1 mL calibrated gas bulb, excess) was added, and the mixture was stirred at ambient temperature for 2 h. The solvent was removed in vacuo to give 22 mg of (56%) of (η^5-C$_5$Me$_4$H)$_2$Hf(OMe)(Tf) (**2-(OMe)Tf**) as a white solid. Anal. Calcd for $C_{20}H_{29}F_3SO_3Hf$: C, 41.06; H, 5.00. Found: C, 41.12; H, 5.12. ^{1}H NMR (benzene-*d*$_6$, 23 °C): δ 1.76 (s, 6H, C$_5$Me$_4$H), 1.78 (s, 6H, C$_5$Me$_4$H), 1.79 (s, 6H, C$_5$Me$_4$H), 1.92 (s, 6H, C$_5$Me$_4$H), 3.89 (s, 3H, Hf-OCH$_3$), 5.46 (s, 2H, C$_5$Me$_4$H). {^{1}H}^{13}C NMR (benzene-*d*$_6$, 23 °C): δ 11.03, 11.37, 12.90, 13.03 (C$_5$*Me*$_4$H), 57.97 (O*C*H$_3$), 111.19, 116.14, 117.58, 123.14, 126.14 (*Cp*), CF$_3$ resonance not located. ^{19}F NMR (benzene-*d*$_6$, 23 °C): δ −85.53 (C*F*$_3$).

Preparation of (η^5-C$_5$Me$_4$H)$_2$Zr(OTf)(η^2-N(CH$_3$)*N*=C(H)-COOEt) (5). In a 20 mL scintillation vial, ethyl diazoacetate (22.3 μL, 0.211 mmol) was added to a solution of 0.070 g of **1-Me$_2$** (0.192 mmol) in approximately 10 mL of toluene. The reaction mixture was stirred at room temperature for 16 h, and the solvent was removed in vacuo. The resulting yellow oil was redissolved in approximately 5 mL of toluene and 54.2 mg of AgOTf (0.211 mmol) was added, whereupon the reaction turned dark brown. The reaction mixture was stirred for 30 min the solvent removed in vacuo and the resulting brown residue extracted with pentane. Following filtration to remove Ag^0 precipitate, recrystallization at −35 °C afforded 0.60 g (51%) of (**5**) as a white solid. Anal. Calcd for $C_{24}H_{35}F_3N_2O_5SZr$: C, 47.11; H, 5.77; N, 4.58. Found: C, 46.84; H, 5.59; N, 4.24. ^{1}H NMR (benzene-*d*$_6$, 23 °C): δ 1.05 (t, $^3J_{HH}$ = 6.7 Hz, 3H, COOCH$_2$C*H*$_3$), 1.58 (s, 6H, C$_5$*Me*$_4$H), 1.82 (s, 6H, C$_5$*Me*$_4$H), 1.89 (s, 6H, C$_5$*Me*$_4$H), 1.95 (s, 6H, C$_5$*Me*$_4$H), 2.98 (s, 3H, N−C*H*$_3$), 4.08 (q, $^3J_{HH}$ = 6.7 Hz, 2H, COOC*H*$_2$CH$_3$), 5.75 (s, 2H, C$_5$Me$_4$*H*), 6.33 (s, 1H, C*H*). {^{1}H} ^{13}C NMR (benzene-*d*$_6$, 23 °C): δ 11.27, 11.68, 13.03, 13.77 (C$_5$*Me*$_4$H), 15.14 (*C*H$_3$), 32.70 (N-*C*H$_3$), 59.76 (*C*H$_2$), 108.63 (Cp), 111.90 (*C*H), 115.47, 115.98, 118.56, 122.76 (Cp), 164.86 (*C*O). ^{19}F NMR (benzene-*d*$_6$, 23 °C): δ −76.53.

Preparation of (η^5-C$_5$Me$_4$H)$_2$Hf(OTf)(η^2-N(CH$_3$)*N*=C(H)-COOEt) (6). In a 20 mL scintillation vial, ethyl diazoacetate (18.0 μL, 0.170 mmol) was added to a solution of 0.070 g of **2-Me$_2$** (0.155 mmol) in approximately 10 mL of toluene. The reaction mixture was stirred at room temperature for 16 h, and the solvent was removed in vacuo. The resulting yellow oil was redissolved in approximately 5 mL of toluene, and 43.7 mg of AgOTf (0.170 mmol) was added, whereupon the reaction turned dark brown. The reaction mixture was stirred for 30 min the solvent removed in vacuo and the resulting brown residue extracted with pentane. Following filtration to remove Ag^0 precipitate, recrystallization at −35 °C afforded 0.071 g (66%) of (**6**) as a white solid. Anal. Calcd for $C_{24}H_{35}F_3HfN_2O_5S$: C, 41.23; H, 5.05; N, 4.01. Found: C, 40.92; H, 4.79; N, 3.74. ^{1}H NMR (benzene-*d*$_6$, 23 °C): δ 1.04 (t, $^3J_{HH}$ = 7.3 Hz, 3H, COOCH$_2$C*H*$_3$), 1.65 (s, 6H, C$_5$*Me*$_4$H), 1.86 (s, 6H, C$_5$*Me*$_4$H), 1.94 (s, 6H, C$_5$*Me*$_4$H), 2.03 (s, 6H, C$_5$*Me*$_4$H), 2.96 (d, *J* = 1.1 Hz, 3H, N−C*H*$_3$), 4.07 (q, $^3J_{HH}$ = 7.3 Hz, 2H, COOC*H*$_2$CH$_3$), 5.73 (s, 2H, C$_5$Me$_4$*H*), 6.43 (d, *J* = 1.1 Hz, 1H, C*H*). {^{1}H} ^{13}C NMR (benzene-*d*$_6$, 23 °C): δ 11.18, 11.72, 12.67, 13.11 (C$_5$*Me*$_4$H), 14.89 (*C*H$_3$), 36.01 (N-*C*H$_3$), 60.37 (*C*H$_2$), 113.03 (Cp), 114.44 (*C*H), 116.40, 121.94, 122.23, 128.92 (Cp), 164.13 (*C*O). ^{19}F NMR (benzene-*d*$_6$, 23 °C): δ −76.27.

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Supporting Information Available: Crystallographic data for **[2-OTf]$_2$N$_2$** in CIF format; representative multinuclear NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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