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Dinitrogen Silylation and Cleavage with a Hafnocene Complex

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S *Supporting Information*

ABSTRACT: Silylation of a hafnocene complex containing a strongly activated dinitrogen ligand, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, by addition of $CySiH_3$ resulted in N−Si and Hf−H bond formation and a compound poised for subsequent N_2 cleavage. Warming the silane addition product to 75 °C triggered N−N scission, for which the requisite electrons were provided by silyl migration. Dinitrogen cleavage coupled to N−C bond formation was also accomplished by carbonylation of the silylated product, yielding an unprecedented μ-formamidide ($[NC(H)O]^{2-}$) ligand. Subsequent treatment with HCl yielded free formamide, demonstrating that an important organic molecule can be synthesized from N_2, CO, an organosilane, and protons.

Homogeneous transition-metal complexes that couple cleavage of the strong N≡N bond (BDE = 225 kcal/mol) of molecular nitrogen to subsequent N−H or N−C bond-forming steps continue to be of interest as a possible direct route to amines, heterocycles, and other value-added N-containing organic molecules.[1] The Chatt cycle,[2] whereby coordinated dinitrogen is functionalized by successive addition of protons and electrons, is a long-standing method for N_2 functionalization and cleavage, and adaptations to other electrophiles have been reported.[3,4] Schrock, and more recently Nishibayashi, have evolved this method into catalytic cycles for ammonia synthesis with 4 and 6 total turnovers per molybdenum (with each turnover yielding two NH_3), respectively.[5] Another possibility is bimetallic N_2 cleavage[6−8] followed by functionalization of the resulting metal nitrido.[9,10] In this approach, the six electrons required for N≡N cleavage are supplied by the two metal centers.

An alternative strategy for dinitrogen functionalization is "ligand-induced" N_2 cleavage, whereby the required six electrons are supplied by a combination of the metals and incoming ligands. This possibility offers tremendous flexibility given the number of metal−ligand combinations that are available to promote N_2 functionalization and cleavage. Fryzuk has successfully demonstrated the viability of this approach and reported several examples of N_2 cleavage and functionalization upon treatment of a ditantalum dinitrogen complex with alanes, boranes, and a zirconium hydride.[11] Our laboratory has recently extended this concept to group 4 metallocene chemistry and has discovered methods for CO-induced N_2 bond cleavage by zircononcene[12] and hafnocene[13] complexes with strongly activated side-on bound N_2 ligands. Building upon the precedent of Sobota,[14] these reactions assemble new N−C and C−C bonds from diatomics with two of the strongest bonds in chemistry and provide a platform for the synthesis of various organic amides directly from N_2.

Dinitrogen silylation has also proven an effective strategy for N_2 functionalization and cleavage. With the side-on, end-on tantalum dinitrogen compound, Fryzuk[15,16] has demonstrated N−Si bond formation with primary and secondary silanes accompanied by N−N bond cleavage. In group 4 chemistry, Fryzuk[17] and Sita[18] have observed N−Si and bridging metal hydride formation from addition of silanes to strongly activated metal compounds with side-on bound dinitrogen ligands. Gambarotta[19] has also described N−Si bond formation from addition of Me_3SiCl to a μ-nitrido, μ-amido titanium anion.

Because of the known rich chemistry of silicon hydrides, we sought to explore the possibility of ligand-induced N_2 cleavage and functionalization chemistry using silanes and hafnocene complexes containing strongly activated side-on bound dinitrogen ligands. Addition of a primary silane such as $PhSiH_3$, $^nBuSiH_3$ or $CySiH_3$ to benzene-d_6 solutions of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$[20] or the *ansa*-hafnocene dinitrogen complex $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$[13] afforded complex, intractable mixtures of products.

As part of our continuing efforts to develop structure-reactivity relationships in group 4 metallocene N_2 chemistry,[21] we sought to prepare new hafnocene dinitrogen complexes with more strongly activated and perhaps more reactive dinitrogen ligands. We postulated that removing additional methyl groups from the $[(\eta^5\text{-}C_5Me_4H)_2Hf]$ scaffold might reduce the steric pressure in the corresponding bimetallic dinitrogen complex, which would result in greater overlap of the metal orbitals with the N_2 π^* orbitals,[22] thereby increasing dinitrogen reduction and ideally the reactivity. Stirring $(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2HfI_2$[23] with excess 0.5% Na(Hg) in toluene under a dinitrogen atmosphere followed by filtration, solvent removal, and recrystallization from pentane at −35 °C furnished a 41% yield of a dark-purple solid identified as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (Scheme 1).

The hafnocene dinitrogen complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, was characterized by ^1H, ^{13}C, and ^{15}N NMR spectroscopy, electronic spectroscopy, combustion analysis, and X-ray diffraction. The ^{15}N isotopologue was prepared by reduction under $^{15}N_2$ and exhibited an ^{15}N NMR resonance centered at 570.20 ppm in benzene-d_6. The solid-state structure (Figure 1 left) confirmed the formation of a hafnocene compound with a side-on bound dinitrogen ligand. The N−N bond distance of 1.457(5) Å is longer than the value of 1.423(11) Å in $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ and identical to the N−N bond length of 1.457(5) Å in the *ansa*-hafnocene dinitrogen

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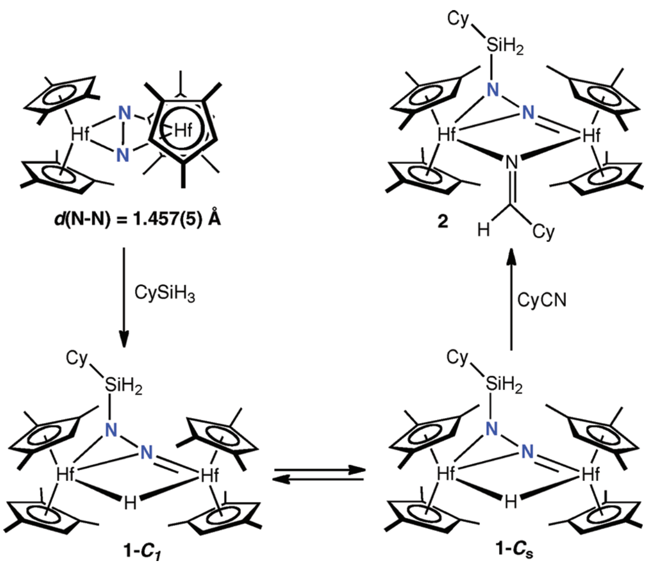
Scheme 1



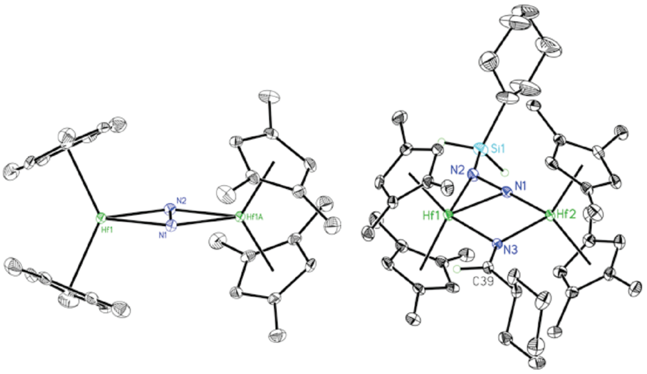


Figure 1. Representations of the solid-state structures of (left) $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ and (right) **2** using 30% probability ellipsoids. Solvent molecules and hydrogen atoms (except those attached to C39 and Si1) have been omitted for clarity. Selected bond distances (Å) for **2**: N1−N2, 1.412(5); Hf1−N1, 2.167(3); Hf1−N2, 2.128(4); Hf1−N3, 2.297(3); Hf2−N1, 1.921(4); Hf2−N3, 2.216(3); N3−C39, 1.274(5).

compound $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$. More reliably, the calculated Hf−Hf distance in $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ is 3.8527(3) Å, which is statistically shorter than the corresponding value of 3.9099(5) Å in $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$. Likewise, a ligand-to-metal charge transfer (LMCT) band of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ was located at 848 nm, which is blue-shifted from the value of 886 nm reported for $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$. Both the crystallographic and spectroscopic data support the hypothesis that removing additional methyl groups from the $[(\eta^5\text{-}C_5Me_4H)_2Hf]$ scaffold increases N_2 reduction.

Addition of 1 equiv of $CySiH_3$ to a diethyl ether solution of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ furnished a brown solid identified as an equimolar mixture of two isomers of a dihafnocene product, which were designated as **1-C$_1$** and **1-C$_s$** (Scheme 1). The isomeric products arose from different orientations of the cyclopentadienyl methyl groups within the bimetallic compound. Assignments of the individual isomers as well as identification of the exchange between them were established by a series of two-dimensional NMR experiments, the details of which are reported in the Supporting Information.

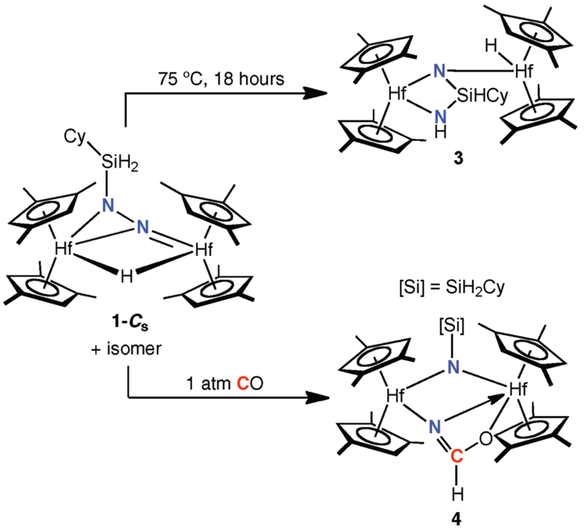
The benzene-d_6 ^1H NMR spectrum of the product mixture of **1-C$_1$** and **1-C$_s$** exhibited diagnostic resonances at 4.97 (**1-C$_1$**) and 4.78 (**1-C$_s$**) ppm, signaling the formation of a μ-hydride ligand in each isomer. The combination of ^{15}N and ^{29}Si NMR spectroscopies established the silylation of the coordinated N_2 to form a side-on, end-on diazenido ligand, similar to the structure and reactivity reported by Sita.[9] For the C_1 isomer, the benzene-d_6 ^{15}N NMR spectrum exhibited a broadened resonance centered at 183.23 ppm for the silylated nitrogen and a doublet ($^1J_{N-N}$ = 13.3 Hz) at 320.97 ppm for the remaining N atom. Similar peaks were observed at 183.98 and 317.05 ($^1J_{N-N}$ = 12.9 Hz) for the C_s isomer.

Although structural confirmation of **1-C$_1$** and **1-C$_s$** has been elusive, we sought to elaborate the μ-hydride into another bridging ligand that would preserve the structure but prove to be more amenable to X-ray diffraction. Addition of 1 equiv of cyclohexanecarbonitrile to a toluene solution of a mixture of the **1-C$_1$** and **1-C$_s$** isomers followed by solvent removal and subsequent recrystallization from a toluene/pentane mixture at −35 °C furnished a 42% yield of purple prisms identified as a single isomer of the nitrile insertion product, **2** (Scheme 1). The side-on, end-on silyldiazenido ligand remained intact and exhibited two doublets ($^1J_{N-N}$ = 11.9 Hz) at 79.80 and 304.45 ppm for the silylated and bridging nitrogens, respectively, in the benzene-d_6 ^{15}N NMR spectrum. The newly formed μ-aldimide ligand exhibited a diagnostic downfield ^1H NMR resonance at 8.46 ppm and a strong N═C band at 1702 cm^{-1} in the benzene solution IR spectrum.

The solid-state structure of **2** was determined by X-ray diffraction (Figure 1 right), and the crystallographic data confirmed the presence of the side-on, end-on diazenido ligand and the formation of the μ-aldimide. The N1−N2 distance of 1.412(5) Å is comparable to the value of 1.422(5) Å reported by Sita for a related dihafnium diazenido compound with a hydride but is contracted relative to that for $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$.[9] The relatively short Hf2−N1 distance of 1.921(4) Å is suggestive of imido character in the hafnium−nitrogen bond. The cyclopentadienyl ligands are geared in an alternating arrangement, placing the unique methyl groups on opposite sides of the molecule. The side-on, end-on coordination of the silyldiazenido ligand may impart stability to **1-C$_1$** and **1-C$_s$** (as well as **2**) and is likely the origin of the clean reactivity observed with $CySiH_3$ and $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$. In hafnocene dinitrogen complexes with more sterically crowded cyclopentadienyls, this coordination mode may not be accessible for the silyldiazenido ligand, resulting in decomposition upon silane addition.

With a hafnocene complex containing a silyldiazenido ligand prepared from N_2 functionalization in hand, methods to cleave the N−N bond were explored. Heating a toluene solution of a mixture of **1-C$_1$** and **1-C$_s$** to 75 °C for 24 h followed by recrystallization from diethyl ether at −35 °C furnished bright-yellow crystals of a new dihafnium compound, **3**, in 49% yield (Scheme 2). The benzene-d_6 ^1H NMR spectrum of **3** exhibited a downfield signal at 9.76 ppm diagnostic of a terminal hafnium hydride.[24] A resonance centered at 2.28 ppm was assigned as an N−H proton, and this assignment was confirmed by performing the silylation with $CySiD_3$ followed by thermolysis and analysis

Scheme 2



by both ^{1}H and ^{2}H NMR spectroscopy. The ^{15}N NMR spectrum of the ^{15}N isotopologue, **3-^{15}N**, exhibited signals at 106.57 and 281.40 ppm with no N–N coupling, confirming the cleavage of the N–N bond.

The solid-state structure of **3** (Figure 2 left) was determined by X-ray diffraction, which established the cleavage of the N–N bond along with the formation of a hafnocene having a terminal hydride ligand. Silyl migration accompanied the N–N bond cleavage reaction, similar to the observations reported by Fryzuk in tantalum dinitrogen chemistry.[11] In **3**, the newly formed [NSi(H)CyNH]$^{3-}$ fragment is in one part analogous to an amide, having hydrogen and silyl substituents, while the environment of the second nitrogen is more unusual and is analogous to a bridging imide, formally serving as a monoanionic donor to both hafnium atoms. Because both of the metal centers in both **1-C_1** and **1-C_s** are Hf(IV) with d^0 configurations, the silyl and hydride migrations must have been the source of the electrons required to cleave the N–N bond.

The observation of N–N bond cleavage resulting from silyl migration upon thermolysis of **1** raised the possibility that exogenous ligands may also be used to promote N$_2$ cleavage. On the basis of our previous success with carbon monoxide,[12,13] a toluene solution of **1-C_1** and **1-C_s** was treated with 1–4 atm CO, and a new hafnocene product, **4**, was isolated in 80% yield as a white powder (Scheme 2). The spectral features of **4** are diagnostic of N–N scission and N–C bond formation. The benzene-d_6 ^{1}H NMR spectrum of **4** exhibited a downfield signal at 9.36 ppm for the hydrogen on the newly formed μ-[NC(H)O]$^{2-}$ ligand that was split into a doublet of doublets ($^1J_{\mathrm{C-H}}$ = 185.5 Hz, $^2J_{\mathrm{N-H}}$ = 8.8 Hz) upon preparation of the ^{13}C,^{15}N isotopologue. The {^{1}H}^{13}C NMR spectrum of **4-^{13}C,^{15}N** exhibited a doublet ($^1J_{\mathrm{N-C}}$ = 8.5 Hz) centered at 169.5 ppm, also confirming N–C bond formation arising from CO-induced N$_2$ cleavage. Accordingly, the ^{15}N NMR spectrum exhibited a resonance at 215.89 ppm for the μ-silylimido ligand and a peak at 283.14 ppm for the μ-[N=CH–O] fragment.

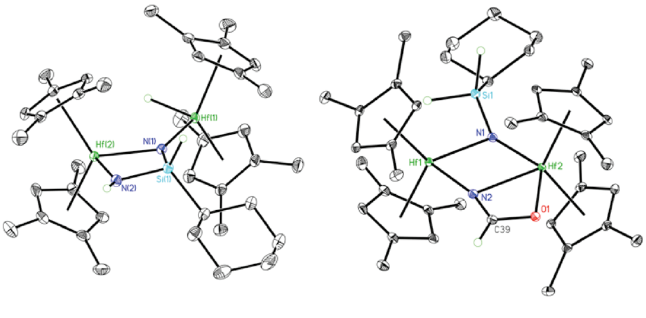
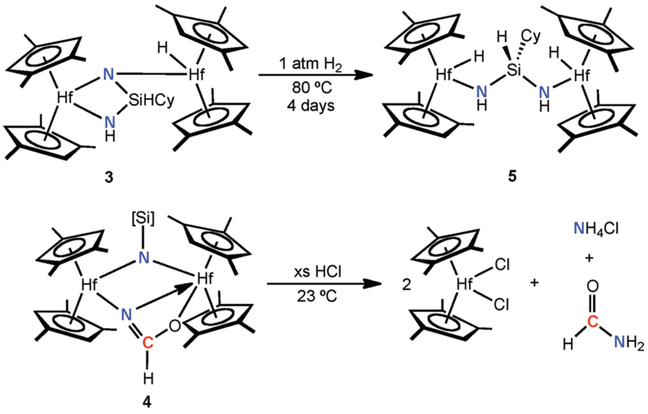


Figure 2. Representations of the solid-state structures of the dinitrogen cleavage products (left) **3** and (right) **4** using 30% probability ellipsoids. Solvent molecules and hydrogen atoms (except those attached to nitrogen, silicon and C39) have been omitted for clarity.

Scheme 3



The solid-state structure of **4** (Figure 2 right) was determined by X-ray diffraction and confirmed the N–N bond cleavage and N–C bond formation upon carbonylation of the mixture of **1-C_1** and **1-C_s**. The cyclopentadienyl methyl groups of each hafnocene are in an eclipsed orientation and are geared across the dimer. The Hf1–N1 and Hf2–N1 distances [2.123(2) and 2.158(2) Å, respectively] are consistent with a bridging imido, while the N2–C39 and C39–O1 distances [1.290(3) and 1.300(3) Å, respectively] indicate double-bond character in the N–C bond of the μ-[NC(H)O]$^{2-}$ ligand. We term this new fragment "formamidide" because it is the dianionic conjugate base of the organic molecule formamide. In **4**, the Hf1–N2 and Hf2–N2 distances [2.080(2) and 2.282(2) Å, respectively] demonstrate the unsymmetrical bonding mode of the formamidide nitrogen. To our knowledge, complexes with μ-[NC(R)O]$^{2-}$ ligands have not previously been prepared or structurally characterized. Related examples are μ-[N(Ar)C(R)O]$^-$ (Ar = aryl) fragments synthesized from addition of aryl isocyanates to ruthenium[25] and osmium[26,27] hydrido carbonyl clusters.

The observation of N–N bond cleavage upon thermolysis or carbonylation of **1-C_1** and **1-C_s** prompted preliminary studies of the reactivities of **3** and **4** with the goal of liberating the functionalized nitrogen products from the hafnium centers. Heating a toluene solution of **3** to 80 °C in the presence of 1 atm H$_2$ for 4 days resulted in a rare example of hydrogenolysis of a Hf–N bond to form the dimeric hafnocene silyl amide hydride, **5** (Scheme 3). Terminal hydrides were located downfield at 9.93 ppm in the benzene-d_6 ^{1}H NMR spectrum, along with Si–H at 5.21 ppm and equivalent N–H's ($^1J_{\mathrm{N-H}}$ = 56.1 Hz) at 4.04 ppm. In the IR spectrum, an N–H stretch was observed at 3437 cm^{-1}, which shifted to 3433 cm^{-1} in the ^{15}N isotopologue. The ^{15}N NMR spectrum exhibited a single resonance centered at 164.55 ppm, and correlation to the N−H resonance at 4.04 ppm was established in an $^1H-^{15}N$ HSQC experiment. The ^{29}Si NMR spectrum of the ^{15}N isotopologue **5-^{15}N** contained a triplet centered at −10.62 ppm ($^1J_{Si-N}$ = 9.0 Hz).

The assembly of coordinated formamide from N_2, silane, and CO prompted us to explore its release from the dihafnium core. Addition of Brønsted acids such as gaseous HCl to a benzene-d_6 solution of **4** resulted in liberation of free formamide, NH_4Cl, and the hafnocene dichloride $(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2HfCl_2$. The NH_4Cl product likely arose from initial formation of silylamine, which was then cleaved and protonated under the acidic conditions to yield ammonium chloride.

In summary, silylation of a hafnocene complex with a strongly activated, side-on bound dinitrogen ligand has been achieved, opening a pathway for subsequent N_2 functionalization and cleavage chemistry. Cleavage of the N−N bond was accomplished by thermal silyl migration or carbonylation under ambient conditions. The latter reaction allowed the synthesis of an organic nitrogen compound, formamide, from N_2, CO, an organosilane, and protons. The new chemistry observed herein likely derives from the accessibility of side-on or end-on, side-on intermediates resulting from a less hindered hafnocene derivative.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete experimental details, representative NMR spectra, and crystallographic data (CIF) for $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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