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Synthesis of a Base-Free Hafnium Nitride from N_2 Cleavage: A Versatile Platform for Dinitrogen Functionalization

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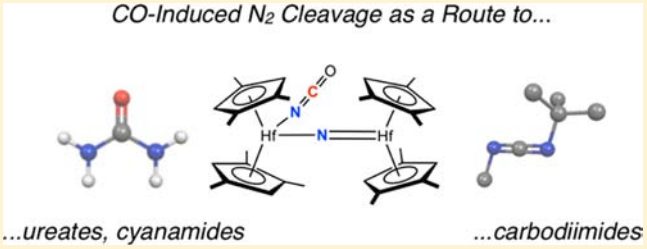
Supporting Information

ABSTRACT: The synthesis and characterization of a metastable, base-free isocyanato dihafnocene μ-nitrido complex from CO-induced dinitrogen cleavage is described. The open coordination site at hafnium suggested the possibility of functionalization of the nitrogen atom by cycloaddition and insertion chemistry. Addition of the strained, activated alkyne, cyclooctyne, resulted in N−C bond formation by cycloaddition. The alkyne product is kinetically unstable engaging the terminal hafnocene isocyanate and promoting deoxygenation and additional N−C bond formation resulting in a substituted cyanamide ligand. Group transfer between hafnium centers was observed upon treatment with Me_3SiCl resulting in bridging carbodiimidyl ligands. Amidinato-type ligands, $[NC(R)N]^{3-}$ were prepared by addition of either cyclohexyl or isobutyronitrile to the base free dihafnocene μ-nitrido complex, which also engages in additional N−C bond formation with the terminal isocyanate to form bridging ureate-type ligands. Heterocummulenes also proved reactive as exposure of the nitride complex to CO_2 resulted in deoxygenation and N−C bond formation to form isocyanate ligands. With substituted isocyanates, cycloaddition to the dihafnocene μ-nitrido was observed forming ureate ligands, which upon thermolysis isomerize to bridging carbodiimides. Taken together, these results establish the base free dihafnocene μ-nitrido as a versatile platform to synthesize organic molecules from N_2 and carbon monoxide.



INTRODUCTION

The functionalization and cleavage of molecular nitrogen is a long-standing challenge in synthesis.[1−4] While the Haber-Bosch process[5,6] and the nitrogenase family of enzymes[7−9] provide industrial and biological routes to ammonia,[10] respectively, catalytic methods for the synthesis of more complex organic nitrogen compounds directly from N_2 are less common.[11] Methods for the catalytic silylation of dinitrogen have been reported using titanium,[12] chromium,[13] molybdenum,[14] tungsten,[14] and most recently iron precursors.[15] In the titanium examples, the method was adapted for the synthesis of heterocycles[16] and natural products including monomorine I, pumiliotoxin C, and lycopodine.[17]

Despite these advances in N−H and N−Si bond formation, methods for nitrogen−carbon bond formation, particularly coupled to N_2 cleavage, have proven to be a more formidable challenge. Selected examples of alkylation[18] and acylation[19,20] of N_2-derived metal nitrides are known but remain rare. Ligand-induced N_2 cleavage, whereby an incoming ligand is responsible for both delivering reducing equivalents and serving as a reagent for forming new bonds to nitrogen, has emerged as a promising strategy for N−C bond formation. Pioneering work by Sobota and co-workers reported the synthesis of titanium isocyanates following the carbonylation of N_2 in the presence of $TiCl_4$-magnesium mixtures.[21] More recently, Fryzuk and co-workers have extended this approach to tantalum dinitrogen chemistry and established that hydride sources such as alanes,[22] silanes[23] and boranes[24,25] are effective ligands for cleavage of the side-on, end-on coordinated N_2 ligand. The resulting putative μ-nitrido ditantalum compound has proven quite reactive, often engaging in P−N bond forming chemistry with the supporting amide-phosphine ligand.[26]

Our laboratory has extended this concept to strongly activated, side-on bound dinitrogen complexes of zirconium and hafnium.[27,28] Carbonylation of the *ansa*-hafnocene dinitrogen compound, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ resulted in rapid cleavage of the N−N bond with concomitant formation of two N−C bonds and one C−C bond to generate a unique example of a bridging oxamidide ligand.[29] This transformation has proven general among zirconium and hafnium complexes with strongly activated dinitrogen ligands[30,31] and has also provided a versatile platform for the synthesis of various *N*-containing organic molecules including substituted oxamides[32] and formamides.[33,34] A combination of pressure studies, kinetic analysis, isotopic labeling[35] and computational efforts[36,37] support the intermediacy of a bimetallic μ-nitrido intermediate following initial carbonylation and N−N cleavage (Scheme 1).

Because C−H activation of a *tert*-butyl cyclopentadienyl substituent in the *ansa* compound prohibits observation of the dihafnocene μ-nitrido intermediate, a less sterically protected

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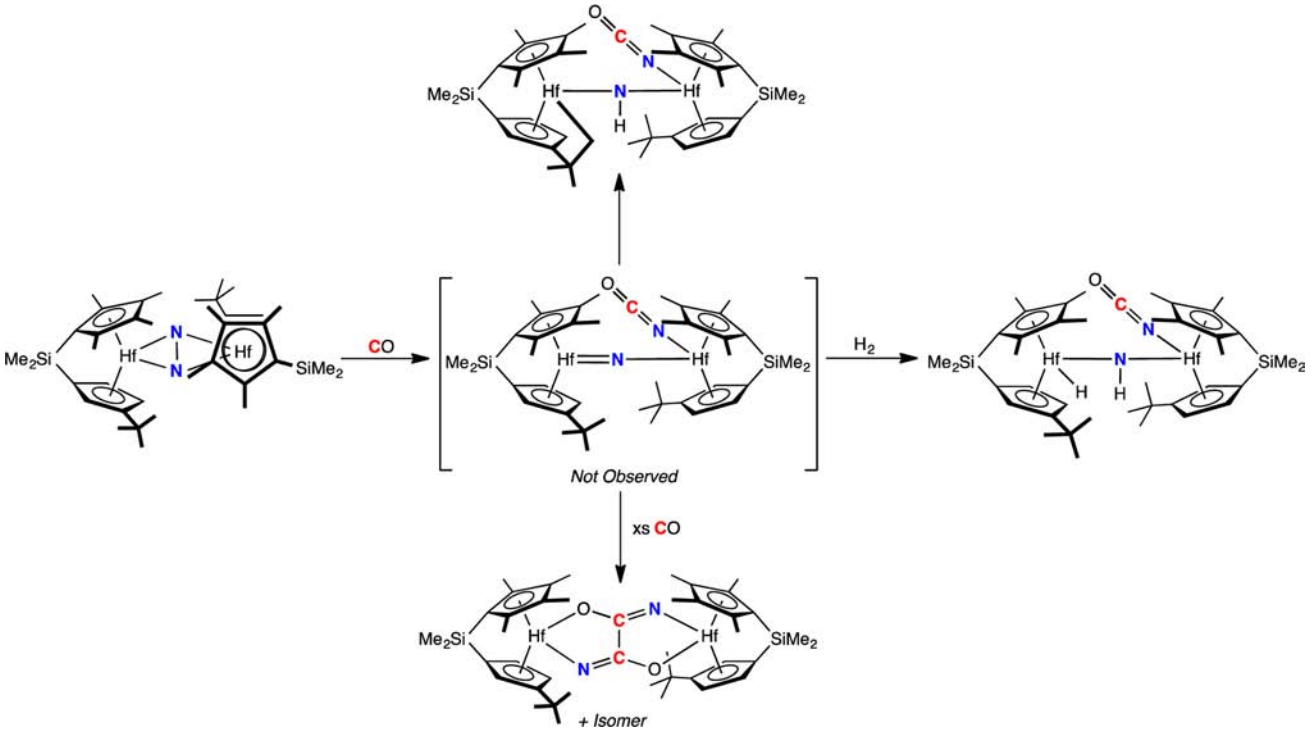
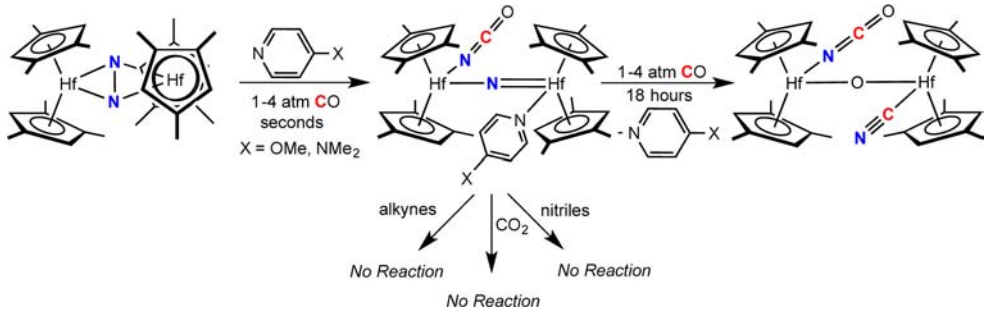
Scheme 1. CO-Induced N_2 Cleavage in an Ansa-Hafnocene Complex That Proceeds through an Unobserved μ-Nitrido Intermediate



Scheme 2. Synthesis of a Pyridine-Stabilized μ-Nitrido Dihafnocene Complex Prepared from N_2 Cleavage



hafnium N_2 complex was studied for dinitrogen carbonylation. Addition of approximately 1 equiv of CO to $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$ in the presence of substituted pyridines such as 4-(dimethylamino)pyridine (DMAP) resulted in isolation and crystallographic characterization of the base-stabilized nitride complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}N)$-(NCO)(DMAP) (Scheme 2).[38] This compound, prepared from N_2 cleavage, is a rare example of a molecular hafnium nitride[39] and serves as a competent intermediate for subsequent carbonylation chemistry to form $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}O)(NCO)(CN)$. Thus, isocyanate and cyanide ligands can be readily accessed from CO-induced N_2 bond cleavage through a bridging nitride intermediate (Scheme 2).

Analysis of the bonding in $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}N)(NCO)(DMAP)$ in conjunction with computational predictions[36] and experimental observations in *ansa*-hafnocene dinitrogen chemistry, suggested that hafnocene nitrides prepared from N_2 cleavage should exhibit a rich reaction chemistry. Transformations such as hydrogenation, C−H activation, alkylation, arylation, and cycloaddition are key and necessary components of synthetic and ideally catalytic schemes for the functionalization of N_2. Unfortunately, the base stabilized compound, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}N)$-(NCO)(DMAP), has proven unreactive in many of these processes, likely a result of the strong coordination of the substituted pyridine ligand which inhibits access to the hafnocene nitrido core (Scheme 2). As a result, the corresponding base free dihafnocene μ-nitrido complex was targeted with the goal of increasing the reactivity of the nitrogen atom relevant to N_2 functionalization. Here we describe the successful synthesis of such a compound and its diverse N−C bond forming chemistry derived from cycloaddition of activated π-systems of an alkyne and heterocummulenes including CO_2 as well as insertion of organic nitriles. In several of these processes, the N−C bond formation at the hafnium-nitride triggers a cascade reaction involving the terminal isocyanate, opening new avenues for functionalization of N-atoms derived from molecular nitrogen. This unique reactivity is likely derived from the appropriate cyclopentadienyl profile, which allows cooperativity between the hafnocene subunits and enables formation of bridging ligands.

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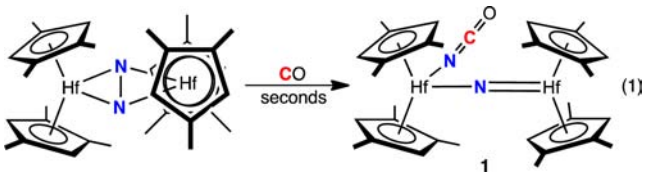
RESULTS AND DISCUSSION

Synthesis of a Base-Free Hafnocene Nitride from N_2 Cleavage. The synthesis of target base-free isocyanato dihafnocene μ-nitrido complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}N)(NCO)$ (**1**) was accomplished by exposure of a frozen benzene-d_6 solution of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$ to 1 equiv of carbon monoxide followed by warming to ambient temperature (eq 1).



Compound **1** proved to be metastable in benzene-d_6 solution decomposing to an intractable mixture of organometallic products over the course of hours ($t_{1/2} \approx 30$ min at 23 °C). Characterization by NMR spectroscopy was conducted immediately following generation of the compound. The benzene-d_6 ^{1}H NMR spectrum of **1** at 23 °C exhibits four broad resonances assigned to the cyclopentadienyl hydrogens and six peaks for the ring methyl groups, consistent with a C_s symmetric compound. The observed broadness in the signals at 23 °C likely arises from restricted cyclopentadienyl ring rotation. Similar behavior has been observed with bimetallic complexes with this cyclopentadienyl ligand array.[34] Cooling a toluene-d_8 solution of **1** to −78 °C resulted in decoalescence of the signals but baseline resolution was not achieved.

Preparation of the ^{13}C, ^{15}N isotopologue, **1-^{13}C, ^{15}N** was accomplished using readily available ^{13}CO and $^{15}N_2$ gas. The benzene-d_6 ^{13}C NMR spectrum exhibits a broad doublet ($^1J_{CN}$ = 35.4 Hz) centered at 131.0 ppm, diagnostic for a terminal isocyanate ligand.[29−35] The ^{15}N NMR spectrum contains two peaks, a doublet centered at 98.2 ppm for the terminal isocyanate and a singlet at 589.9 ppm for the μ-nitrido. These values are similar to the previously reported pyridine stabilized complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(\mu_2\text{-}N)$(4-OMe-pyridine) (**2**).[38] Formation of a terminal isocyanate ligand was also confirmed by solid-state (KBr) infrared spectroscopy, which features an intense band at 2221 cm^{-1}. Additional evidence for synthesis of the base free nitride was obtained from the clean and quantitative generation of **2** from treatment of a benzene-d_6 solution of **1** with 4-methoxypyridine. Likewise, exposure of a benzene-d_6 solution of **1** to 1−4 atm of CO furnished the μ-oxo cyano hafnocene isocyanate described previously.[31]

The bonding in the base-free isocyanato dihafnocene μ-nitrido was analyzed with the assistance of full molecule DFT calculations. The coordinates for the crystallographically characterized, pyridine-stabilized derivative, **2**[38] served as the starting point following deletion of the heterocycle. Attempted geometry optimization resulted in C−H activation of a cyclopentadienyl methyl group in silico, reactivity previously observed with an *ansa*-hafnocene variant.[29] As a result, single point calculations were conducted using the geometry observed in the crystal structure of the pyridine-stabilized complex.

The DFT computed HOMO-1, HOMO, and LUMO for **1** are presented in Figure 1. The HOMO-1 is principally composed of a nitrogen p-orbital in the metallocene wedge interacting weakly with a hafnocene $1a_1$ orbital. Analogous to **2**, the HOMO consists of an orthogonal nitrogen p-orbital

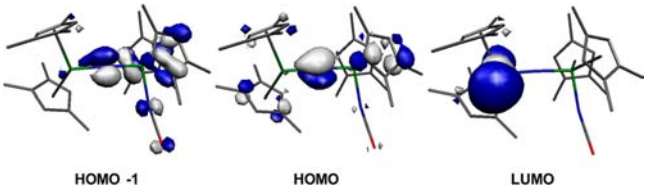


Figure 1. DFT computed HOMO-1, HOMO, and LUMO for **1**.

perpendicular to the hafnocene wedge. Accordingly, this orbital has little interaction with either hafnium. Unlike the pyridine stabilized complex **2**, where the LUMO is centered on the π-system of the aryl ring, the LUMO of the base-free compound is a hafnium $1a_1$ orbital with little to no ligand contribution. The availability of this orbital to interact with incoming ligands accounts for the vastly expanded reactivity of the base-free complex in further N-atom functionalization.

Cycloaddition of Cyclooctyne with 1. The isolation of a base free isocyanate dihafnocene μ-nitrido complex presents new opportunities for N_2 functionalization following cleavage of the N≡N bond. In one limit, the nitrogen atom in **1** can be viewed as an imido and may offer functionalization reactivity by cycloaddition. Imido character in zirconocene and hafnocene complexes bearing strongly activated dinitrogen ligands has also proven useful for preparing N−C bonds by cycloaddition of various heterocummulenes to coordinated N_2.[40−42] Despite the synthesis of numerous zirconium and hafnium complexes with strongly activated N_2 ligands, dinitrogen functionalization and N−C bond formation by alkyne cycloaddition remains rare. Typically, N_2 dissociation and metallocycle formation are observed.[43] One notable exception was reported by Fryzuk,[44] who described addition of terminal, aryl-substituted alkynes to a bis(phosphine) diamido-ligated zirconium dinitrogen complex. CO-induced N_2 cleavage offers an alternative and promising strategy for N−C bond formation by cycloaddition as dinitrogen dissociation pathways are eliminated.

Unactivated olefins and alkynes such as ethylene, butadiene, and 2-butyne proved unreactive toward **1**. However, addition of the strained and activated alkyne, cyclooctyne to a benzene-d_6 solution of **1** furnished a new C_s symmetric dihafnocene product, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(\mu_2,\kappa^2\text{-}N\text{-}(cyclooctenyl))$ (**3**) in 59% yield following recrystallization (Scheme 3). The benzene-d_6 ^{1}H NMR spectrum of **3** exhibits diagnostic pseudo triplets at 2.36 and 3.03 ppm for the allylic methylene hydrogens from the azametallocycle, consistent with N−C bond formation from alkyne cycloaddition. Additional evidence for formation of an azametallocycle was provided by ^{15}N NMR spectroscopy. The labeled isotopologue, **3-^{15}N/^{13}C** exhibits a doublet ($^1J_{CN}$ = 31.9 Hz) centered at 87.9 ppm for the terminal isocyanate and a singlet, centered at 286.6 ppm from the μ_2,κ^2-cyclooctenyl nitrogen (Figure 2). Formation of a terminal isocyanate ligand was also confirmed by the ^{13}C NMR spectrum of **3-^{15}N/^{13}C**, which exhibited a doublet centered at 135.9 ppm.

Attempts to obtain single crystals of **3** proved challenging as toluene solutions of the compound proved thermally unstable even at −35 °C, converting to a new, C_s symmetric dihafnocene compound, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}O)(\mu_2,\kappa^2\text{-}(cyclooctenyl)N\text{-}C{=}N)$ (**4**), over the course of days. Complete conversion of **3** to **4** was also achieved in two hours upon heating to 65 °C. The ^{1}H NMR spectrum of **4** signals C_s symmetry and importantly, contains all the resonances expected for an intact cyclooctenyl fragment.

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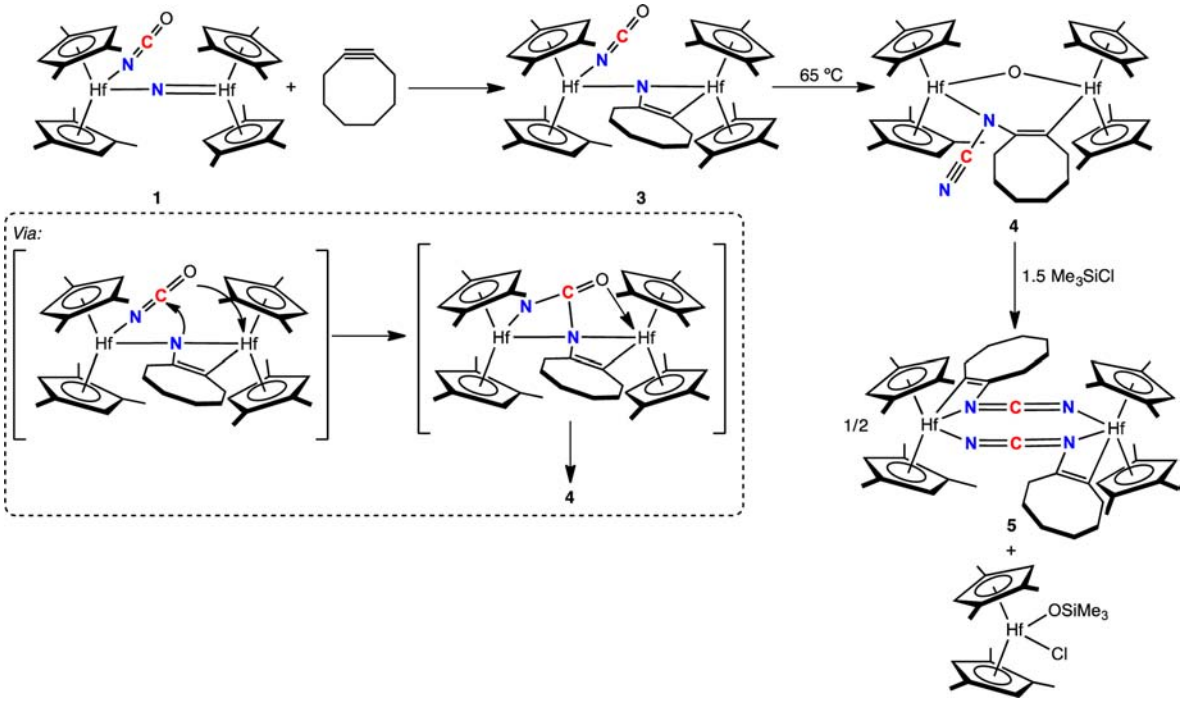
Scheme 3. Cycloaddition of Cyclooctyne to 1 and Subsequent Rearrangement Chemistry



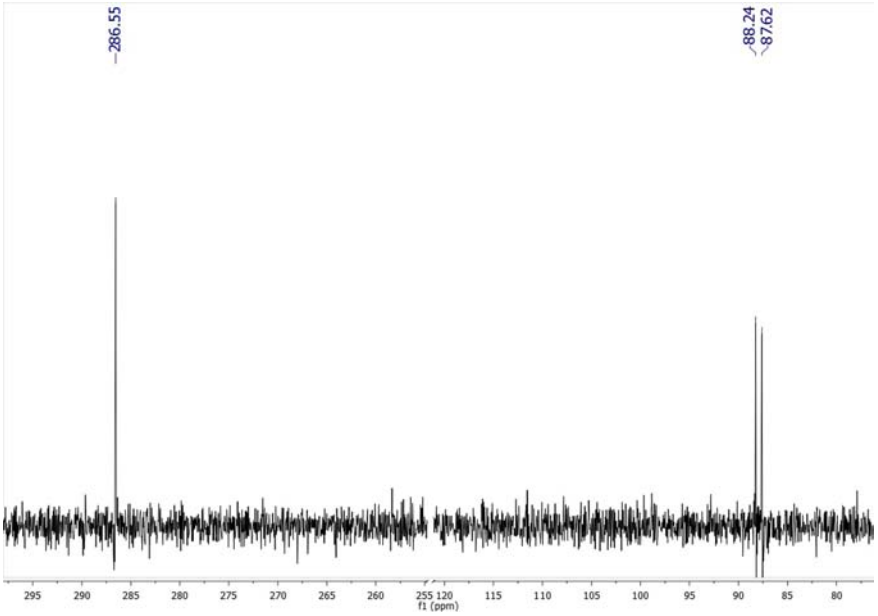


Figure 2. Benzene-d_6 ^{15}N NMR spectrum of **3-^{15}N/^{13}C** at 298 K.

Notably, the ^{15}N NMR spectrum of **4-^{15}N/^{13}C** revealed modification of the hafnium terminal isocyanate, indicating that additional N−C bond forming chemistry had occurred. A new doublet with C−N coupling ($^{1}J_{CN}$ = 13.5 Hz) was observed centered at 208.1 ppm along with a second broad resonance centered at 149.8 ppm. These spectral features are consistent with deoxygenation of the isocyanate ligand and formation of a new *N*-cyanamide-type moiety (Scheme 3). Accordingly, the ^{13}C NMR spectrum of **4-^{15}N/^{13}C** exhibited a broad ($\Delta\nu_{1/2}$ = 79 Hz) resonance at 129.0 ppm, while the solid state (KBr) infrared spectrum contained a broad, intense band at 2094 cm^{-1}, assigned to a stretch of a newly formed *N*-cyanamide ligand.

Single crystals of **4** for suitable for X-ray diffraction were obtained from a toluene/pentane mixture at −35 °C and confirmed isocyanate deoxygenation and additional N−C bond formation (Figure 3). The core of the molecule is a six-membered ring containing two metal centers, a bridging oxide and the C═C−N portion of the newly formed *N*-cyanamide ligand. The C(34)−C(35) distance of 1.322(9) Å is consistent with retention of double bond character in the cyclooctenyl fragment while the C(34)−N(2) distance of 1.489(8) Å is indicative of a carbon−nitrogen single bond. The C(33)−N(3) bond length of 1.152(8) Å is consistent with carbon−nitrogen triple bond character, while the C(33)−N(2) bond length of 1.313(8) Å is indicative of partial double bond character, likely

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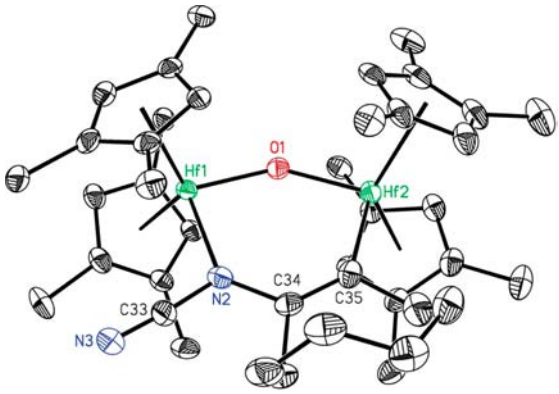

Figure 3. Molecular structure of **4** at 30% probability ellipsoids. Hydrogen atoms and one molecule of toluene omitted for clarity. Selected bond distances (Å): N(2)−C(33) = 1.152(8), N(3)−C(33) = 1.313(8), N(2)−C(34) = 1.489(8), and C(34)−C(35) = 1.322(9).

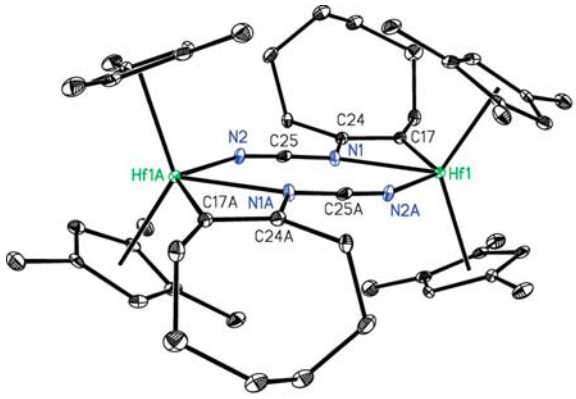

Figure 4. Molecular structure of **5** at 30% probability ellipsoids. Hydrogen atoms and disordered orientation of cyclooctyl ring have been omitted for clarity. One half of the molecule has been generated by symmetry. Selected bond distances (Å): C(17)−C(24) = 1.342(4), N(1)−C(24) = 1.435(4), N(1)−C(25) = 1.281(4), and N(2)−C(25) = 1.163(4).

a result of a delocalized π-system that extends over the cyanamide and cyclooctenyl fragments. The thermal instability of **3** is notable as deoxygenation of a terminal isocyanate ligand triggers a second N−C bond forming reaction and demonstrates that terminal hafnocene isocyanates, prepared from N_2 and CO, may also serve as building blocks for new nitrogen-containing organic ligands.

The conversion of **3** to **4** likely occurs by nucleophilic attack of the nitrogen in the azametallocycle on the carbon of the terminal hafnium isocyanate (Scheme 3). It is interesting to note that cycloaddition of the alkyne maintains nucleophilicity of the nitrogen, allowing it to engage in additional N−C bond forming chemistry. Dexoygenation of the putative ureate-type intermediate to form the observed μ-oxide compound with concomitant formation of the bridging cyanamide ligand is likely driven by release of strain imposed by the metallocycles.

The synthesis of an alkenyl-substituted, *N*-bound cyanamide ligand from CO-induced N_2 cleavage prompted exploration of the reactivity of this fragment with the goal of releasing substituted cyanamides from the coordination sphere of the hafnium. Addition of Me_3SiCl to a benzene-d_6 solution of **4** produced a 2:1 mixture of monometallic and bimetallic products. The monometallic product was identified as (η^5-C_5H_2-1,2,4-Me_3)$_2$Hf(OSiMe_3)Cl based on comparison to an authentic sample independently prepared by treatment of (η^5-C_5H_2-1,2,4-Me_3)$_2$$HfCl_2$ with 1 equiv of NaOSiMe_3. The bimetallic product was identified as the dimeric dihafnocene compound, [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf(μ_2-N═C═N-(cyclooctenyl)]$_2$ (**5**), arising from group transfer of the [N═C═N(cyclooctenyl)]$^{2-}$ ligands between metal centers.

Pure samples of **5** were obtained by fractional crystallization from the reaction mixture using fluorobenzene. Analysis of single crystals by X-ray diffraction established the molecular structure (Figure 4). The asymmetric unit contains one-half of the molecule with an inversion center generating the remainder of the structure. The cyanamide ligand bridges the two hafnium centers and is κ^1 N-bound to one metal and κ^2-C, N bound to the other. The Hf(1)−C(17) and Hf(1)−N(1) bond lengths of 2.342(3) Å and 2.268(2) Å are slightly elongated for X-type ligands. The C(17)−C(24) distance in the cyclooctenyl ring of 1.342(4) Å is consistent with retention of double bond character. The carbodiimidyl fragment exhibits disparate C−N bond distances of 1.281(4) and 1.163(4) Å for C(25)−N(1) and C(25)−N(2) respectively, indicating delocalization of electron density in the azacyclooctenyl fragment. On the basis of the observed metrical parameters, the C(25)−N(2) fragment can be viewed as an L type cyanamide ligand interacting with one hafnium with the azacyclooctenyl fragment acting as an X_2 type donor to the other metal center.

The benzene-d_6 ^{1}H NMR spectrum of **5** displays the expected resonances for a C_{2v} symmetric hafnocene dimer. The observed higher symmetry in solution versus the solid state structure is likely a result of the fluxionality of the 8-membered rings. Multinuclear NMR spectroscopy on the ^{15}N/^{13}C isotopologue **5**-^{15}**N**/^{13}**C** confirmed that the central carbodiimidyl atom was derived from ^{13}CO. The ^{13}C NMR spectrum of **5**-^{15}**N**/^{13}**C** in benzene-d_6 contains an isotopically enhanced doublet of doublets, which is partially obscured by the residual solvent signal (see Supporting Information, SI). Preparing the sample in tetrahydrofuran-d_8 allowed clear observation of the resonance and determination of the two coupling constants to ^{15}N ($^1J_{CN}$ = 30.1, 24.3 Hz). The ^{15}N NMR spectrum of **5**-^{15}**N**/^{13}**C** in benzene-d_6 exhibits an upfield doublet ($^1J_{CN}$ = 24.3 Hz) at 70.2 ppm and another doublet ($^1J_{CN}$ = 30.1 Hz) at 161.3 ppm, which were assigned to N(1) and N(2) respectively.

N−C Bond Formation by Nitrile Insertion. The cycloaddition of the strained alkyne to the μ-nitrido ligand in **1** followed by isocyanate deoxygenation and additional N−C bond formation prompted study of other activated π-systems. Nitriles were interesting targets given their potential for two coordination and hence reactivity modes—one as an L-type ligand from σ-bonding through the nitrogen lone pair and the other from insertion or cycloaddition reactivity engaged through the π-system of the C≡N bond. Addition of 1 equiv of pivalonitrile to a benzene-d_6 solution of **1** resulted in straightforward coordination of the nitrile to form the ligand-stabilized dihafnocene μ-nitride complex, [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(^{t}BuCN)(μ_2-N) (**6**) as judged by NMR spectroscopy and X-ray diffraction. Complete characterization details and a representation of the molecular structure are reported in the SI.

Complex **6** proved to be unstable in solution, decomposing in both benzene and tetrahydrofuran over the course of hours at 23 °C to unidentified organometallic products with no evidence for C−N bond formation. Reasoning that the large

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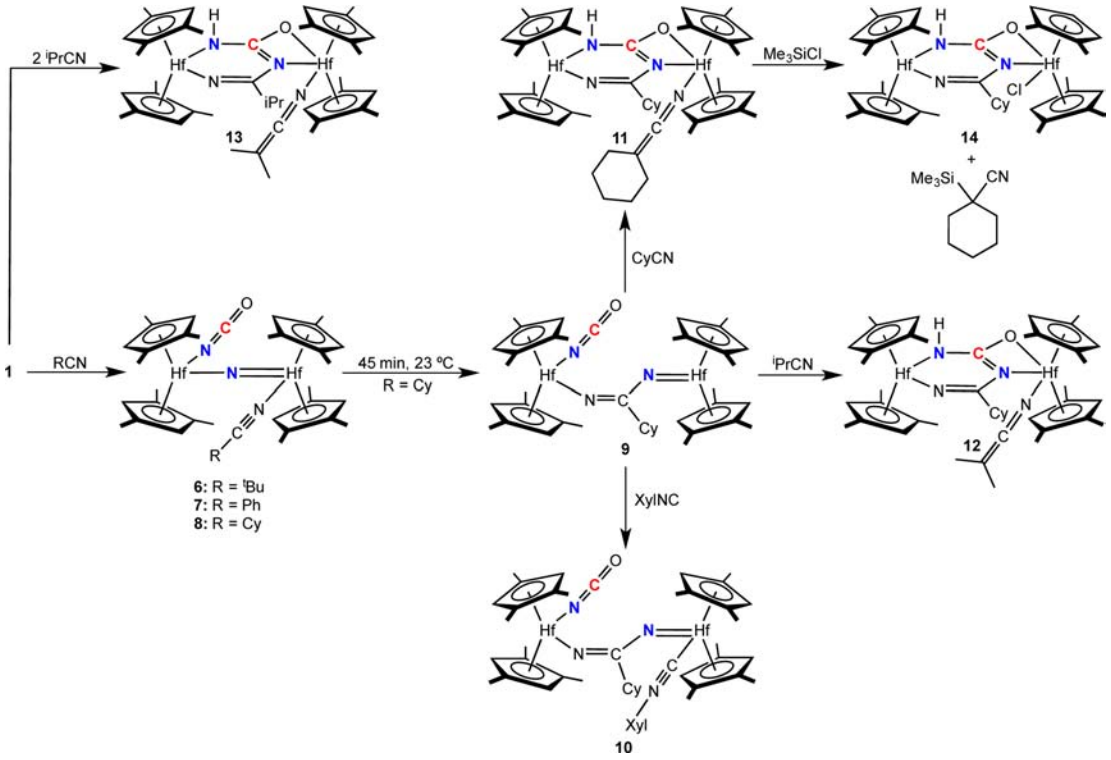
Scheme 4. Reactivity of 1 with Various Organonitriles



tert-butyl substituent inhibited the π-system of the nitrile from engaging in productive chemistry with the μ-nitride, nitriles with smaller substituents were explored. Addition of benzonitrile to **1** again resulted in straightforward coordination to the hafnium, yielding $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(PhCN)(\mu_2\text{-}N)$ (**7**). This compound, like **6** also proved unstable in solution and no productive N−C bond forming chemistry was observed. Addition of excess benzonitrile to **1** also produced **7** but did not result in stabilization of the complex.

Addition of cyclohexanecarbonitrile (CyCN) to a benzene-d_6 solution of **1** resulted in productive chemistry. As with the other nitriles, coordination occurred immediately and the expected ligand-stabilized complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(CyCN)(\mu_2\text{-}N)$ (**8**) was observed as judged by multinuclear NMR spectroscopy. Over the course of approximately 45 min at 23 °C, benzene-d_6 solutions of **8** cleanly and quantitatively converted to a new C_s symmetric dihafnocene complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(\mu_2\text{-}NC(Cy)N)$ (**9**) identified based on a combination of multinuclear NMR and IR spectroscopies (Scheme 4). The ^{13}C NMR spectrum of the doubly labeled isotopologue, **9-^{13}C, ^{15}N** exhibited an isotopically enhanced doublet ($^1J_{CN}$ = 29.0 Hz) centered at 129.0 ppm diagnostic for terminal hafnium isocyanate. A second, natural abundance doublet ($^1J_{CN}$ = 7.9 Hz) was located at 182.6 ppm for the carbon atom of the nitrile. The observed coupling to an isotopically labeled nitrogen confirmed insertion of the unsaturate into the dihafnocene μ-nitrido forming a $[NC(Cy)N]^{3-}$ amidinato ligand. The term amidinato was coined as this fragment is the trianionic version of the well-established monoanionic amidinate ligand.

The ^{15}N NMR spectrum of **9-^{13}C, ^{15}N** exhibits a resonance at 86.7 ppm, ($^1J_{CN}$ = 29.0 Hz) typical for a terminal hafnocene isocyanate. A second resonance was located at 374.0 ppm, significantly upfield shifted from the value of 601.5 ppm observed in the nitrile complex of the nitrido, **8**, assigned as the imido-type nitrogen atom in the $[NC(Cy)N]^{3-}$ ligand. Attempts to obtain single crystals of **9** have been unsuccessful as solutions of **9** underwent decomposition to unidentified products over the course of days at −35 °C. To circumvent decomposition pathways, 1 equiv of 2,6-dimethylphenyl isocyanide was added to a benzene-d_6 solution of **9** and furnished the ligand-stabilized hafnocene product, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(CN\text{-}2,6\text{-}Me_2C_6H_3)(\mu_2\text{-}NC(Cy)N)$ (**10**).

The solid-state structure of **10** was determined by X-ray diffraction and a representation of the molecule is presented in Figure 5. The crystallographic data confirmed insertion of the nitrile into the μ-imido fragment and formation of the $[NC(Cy)N]^{3-}$ ligand. The C−N distances of 1.311(7) and 1.324(7) Å in the amidinato ligand are statistically indistinguishable despite the difference in formal bond order, suggesting a degree of delocalization. Accordingly, the hafnium−nitrogen bonds Hf(2)−N(1) and Hf(1)−N(3) are also nearly identical at 1.932(4) and 1.936(5) Å. The similarity in Hf−N bond distances may arise from contributions from a zwitterionic resonance form, where a formal negative charge is located on N(1) and the corresponding positive charge is localized on Hf(2) while maintaining a Hf−N single bond. This increased charge on N(1) may also explain the further reactivity of this complex (vide infra). While monoanionic amidinate ligands are widely used in coordination and organometallic chemistry including supporting early transition metals that promote N_2 activation and functionalization,[45] this is to the best of our knowledge the first example of such a trianionic, unsubstituted fragment. It is also notable that the nitrile ligand *inserts* into the hafnium imido bond rather than participating in cycloaddition chemistry. Thus, the π-system of the nitrile is

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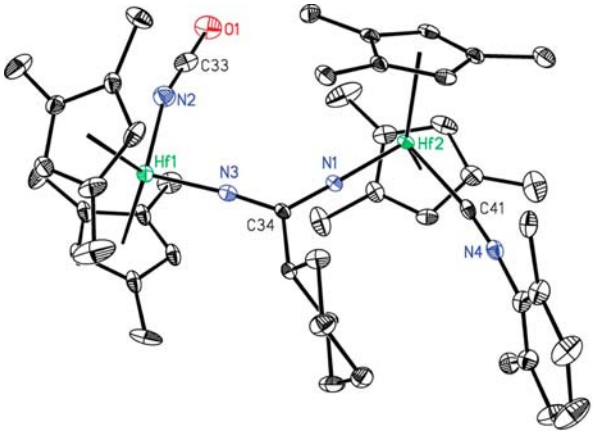

Figure 5. Molecular structure of **10** at 30% probability ellipsoids. Hydrogen atoms and one molecule of benzene solvate omitted for clarity. Selected bond distances (Å): Hf(2)−N(1) = 1.932(4), Hf(1)−N(3) = 1.936(5), N(1)−C(34) = 1.324(7), and N(3)−C(34) = 1.311(7).

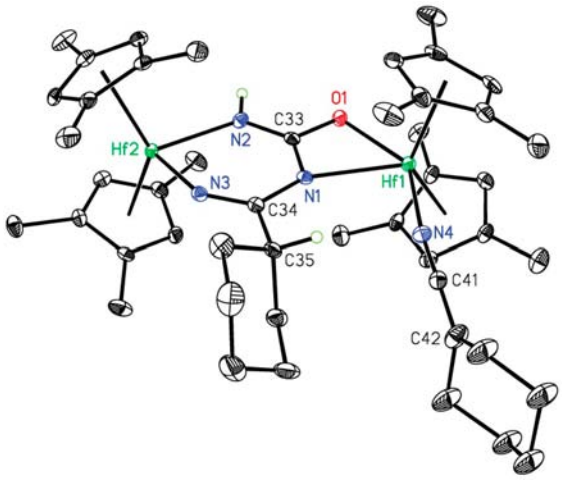

Figure 6. ORTEP plot of **11** at 30% probability ellipsoids. Disordered cyclohexyl carbons and hydrogen atoms (except those attached to N2 and C35) omitted for clarity. Selected bond distances (Å): N(1)−C(33) = 1.353(7), N(1)−C(34) = 1.418(7), N(2)−C(33) = 1.325(7), N(3)−C(34) = 1.281(7), and C(41)−C(42) = 1.344(9).

important for promoting reactivity but distinguishes the chemistry observed with cyclooctyne.

The similar spectral properties between **9** and structurally characterized **10** suggest that despite the similarity in bond distances, in one canonical form, one of the hafnium−nitrogen bonds in **9** may be viewed as having imido-character and offer associated reactivity. Additional nitrogen-element bond formation was of interest as the nitrogen is derived from N_2. Treatment of a benzene-d_6 solution of **9** with a further equivalent of CyCN furnished a new C_s symmetric hafnocene compound, **11** (Scheme 4). A combination of multinuclear NMR spectroscopy, infrared spectroscopy and X-ray diffraction established an additional N−C bond-forming event arising from formal attack of the "imide-like" amidinato nitrogen on the terminal hafnocene isocyanate. This cascade is accompanied by deprotonation of the exogeneous nitrile to form a ketimide ligand with concomitant protonation of the nitrogen from the NCO ligand (Scheme 4).

The ^{15}N NMR spectrum of the doubly labeled isotopologue **11**-^{15}**N**/^{13}**C** exhibits a doublet of doublets ($^1J_{NH}$ = 66.2, $^1J_{CN}$ = 10.1 Hz) centered at 135.1 ppm, confirming N−H bond formation at N(2). The central ureate nitrogen, N(1) was located as a doublet at 392.1 ppm ($^1J_{CN}$ = 1.4 Hz). The cause of the large disparity in C−N coupling constants between the two fragments is unknown at this time. The ^{13}C NMR spectrum of **11**-^{15}**N**/^{13}**C** contains an isotopically enhanced doublet of doublets at 168.8 ppm ($^1J_{CN}$ = 10.1, $^1J_{CN}$ = 1.4 Hz) supporting N−C bond formation via intramolecular attack on the terminal isocyanate. The benzene-d_6 IR spectrum contains an NH band at 3340 cm^{-1} in addition to terminal ketimine and imine C═N stretches at 2056 and 1585 cm^{-1}, respectively.

The solid-state structure of **11** was confirmed by single crystal X-ray diffraction and a representation is shown in Figure 6. The core of the molecule contains an eight membered bicycle composed of four- and six-membered substructures. The two hafnium atoms are essentially coplanar within these ring systems. One hafnocene is coordinated by a formally dianionic N,O-carbodiimidate-type ligand, whereas the other has a coordination sphere containing imidinato and amide coordination. The hydrogen atom attached to N(2) was independently located and the deprotonation of the cyclohexyl methine carbon is clearly indicated by the metrical parameters. The C(41)−C(42) bond distance of 1.344(9) Å is consistent with a carbon−carbon double bond and the bond angles about C(42) are consistent with sp^2 hybridization. The former amide/imide subunit is no longer symmetric, with distinct N(3)−C(34) and N(1)−C(34) bond lengths of 1.281(7) and 1.418(7) Å, consistent with C−N double and single bonds, respectively.

The unique cascade chemistry observed upon addition of a second equivalent of nitrile to **9** prompted exploration of the generality of the transformation. Unlike the other cascade initiated by cyclooctyne cycloaddition, engagement of the terminal hafnium isocyanate does not result in net deoxygenation, instead attack on the central carbon atom results in an anionic oxygen ligand bound to the second hafnium, highlighting the cooperative nature of each metallocene subunit in the bimetallic structure. Of particular interest was whether other nitriles with acidic α-hydrogens would promote similar reactivity. Addition of isobutyronitrile to a benzene-d_6 solution of **9** furnished the C_s symmetric dihafnocene **12**, where cyclohexylnitrile was exclusively incorporated into the extended ureate core and the isobutyronitrile had undergone deprotonation to form the terminal ketimido ligand (Scheme 4). Importantly, there was no evidence by NMR spectroscopy for formation of the isomer derived from cyclohexylnitrile deprotonation, consistent with either irreversible insertion of the first equivalent of nitrile or rapid intramolecular attack on the terminal isocyanate.

Incorporation of isobutyronitrile into the extended ureate core was accomplished by straightforward treatment of **1** with 2 equiv of nitrile at 23 °C and resulted in isolation of **13**. Attempts to observe an intermediate insertion product analogous to **9** by NMR spectroscopy were unsuccessful, demonstrating a rapid deprotonation reaction with isobutyronitrile likely from the reduced steric profile of the nitrile.

The assembly of a unique ureate-type core from CO-induced N_2 splitting followed by nitrile insertion in **11** prompted attempts at further elaboration. Addition of Me_3SiCl to a benzene-d_6 solution of **11** resulted in immediate formation of a new C_s symmetric product, as judged by ^{1}H NMR spectroscopy. The data established disappearance of the cyclohexyl

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resonances for the ketimide ligand with concomitant formation of 1-(trimethylsilyl)cyclohexane-1-carbonitrile, a result of electrophilic attack of the trimethylsilyl group on the ketimide carbon (Scheme 4). The structure of the organometallic product was established as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(Cl)(\mu_2\text{-}NC(Cy)NCN(H)O)$ (**14**) by X-ray diffraction (Figure 7) and confirmed replacement of the ketimide by chloride. Addition of excess Me_3SiCl to **14** produced no reaction.

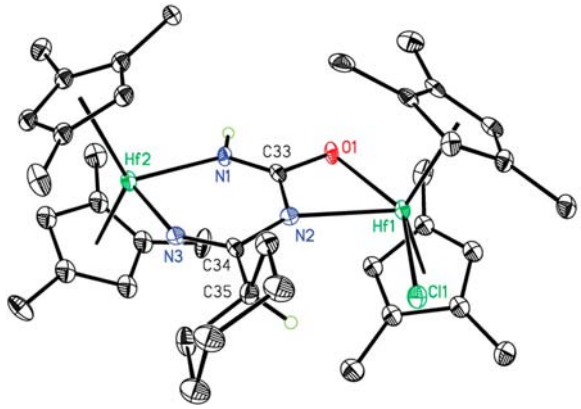
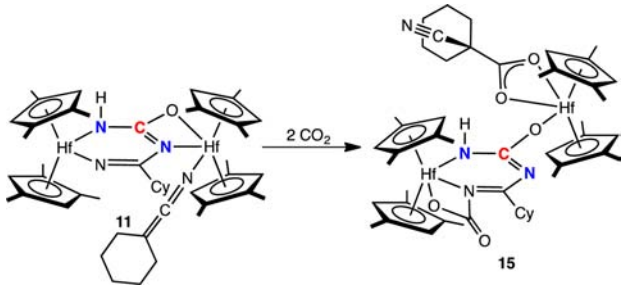


Figure 7. Molecular structure of **14** at 30% probability ellipsoids. Two molecules of tetrahydrofuran solvate and hydrogen atoms (except those attached to N1 and C35) omitted for clarity.

In an attempt to divert reactivity away from ketimide displacement, carboxylation reactions were explored. Exposure of a benzene-d_6 solution of **11** to 2 equiv of CO_2 resulted in rapid formation of a new hafnium product, **15** (Scheme 5).

Scheme 5. Carboxylation of 11



Analysis of the benzene-d_6 ^{1}H NMR spectrum revealed a downfield shift of the N−H proton by approximately 1 ppm, signaling modification of the ureate core. Performing the carboxylation with $^{13}CO_2$ furnished **15**-^{13}**C**$_2$ and the resulting ^{13}C NMR spectrum contained two isotopically enhanced resonances centered at 158.6 and 175.5 ppm. In addition, the methylene carbons of the former ketimide ligand exhibit C−C coupling ($^2J_{CC}$ = 2.9 Hz) to the signal at 175.5 ppm, indicating CO_2 addition occurred at *both* the ureate and ketimide portions of the molecule. Attempts to observe intermediates in the reaction by addition of 1 equiv of CO_2 gas to **11** were unsuccessful and resulted in an approximate equimolar mixture of the starting hafnocene and **15**.

The solid-state structure of **15** was confirmed by a single crystal X-ray diffraction experiment and a representation of the molecule is presented in Figure 8. The structural data establish addition of 1 equiv of CO_2 into the ketimide ligand with concomitant rearrangement to form an unusual carboxylate

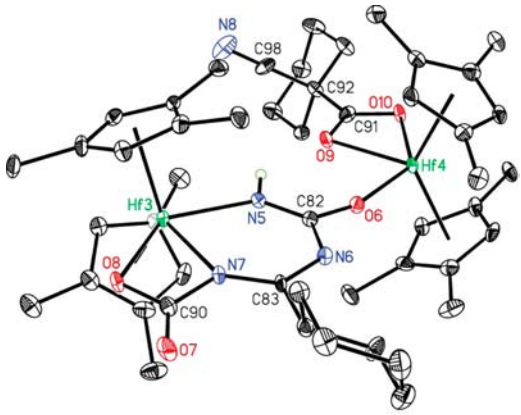


Figure 8. Molecular structure of one of two independent molecules of **15** at 30% probability ellipsoids. Hydrogen atoms (except that attached to N5) and one molecule of toluene solvate omitted for clarity. Selected bond distances (Å): N(5)−C(82) = 1.279(8), N(6)−C(82) = 1.395(7), N(6)−C(83) = 1.327(8), N(7)−C(83) = 1.351(7), N(7)−C(90) = 1.387(8), Hf(3)−N(5) = 2.235(5), and Hf(3)−N(7) = 2.199(5).

ligand. A second independent molecule was located in the asymmetric unit, which differs slightly from the one presented in Figure 8 in that the acetate ligand adopts κ^1 hapticity. In both cases, the carboxylate ligands contain a new C−C bond between the carbon of the CO_2 molecule and the cyclohexane ring of the former ketimide ligand. The second equivalent of CO_2 inserted into the nitrile-derived nitrogen of the ureate core forming a carbamate-type ligand. The combined carboxylation events trigger a change in hapticity of the bridging ureate ligand where in **15** a single oxygen atom forms the linkage between the hafnocene subunits.

Carboxylation of **14** proceeded in a similar manner. Replacement of the ketimide ligand by chloride confines the CO_2 addition to the ureate core and cleanly furnished the dihafnocene product, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(Cl)(\mu_2\text{-}O_2CNC(Cy)NCN(H)O)$ (**16**). The benzene-d_6 ^{13}C NMR spectrum of **16**-^{13}**C**, prepared using $^{13}CO_2$, exhibited an isotopically enhanced resonance centered at 158.4 ppm. Without structural characterization, definitive assignment of the hapticity of the ureate core is challenging.

The reactivity of **9** and **10** with electrophiles was also explored in an attempt to induce group transfer of the ureate-like core. Addition of 1 equiv of Me_3SiCl to a benzene-d_6 solution of either compound cleanly furnished a new C_s symmetric dihafnocene product, **17**. Analysis of the ^{1}H and ^{13}C NMR data established that the product arises from delivery of chloride to one hafnocene subunit which induces intramolecular attack of the imido-like nitrogen on the terminal hafnocene isocyanate. As shown in Scheme 6, initial chloride abstraction by the hafnocene generates a nucleophilic carbodiimidyl nitrogen which attacks the carbon of the terminal isocyanate. Capture of the silyl group generates the observed product, **17**. Notably, additional silylation does not occur at the nitrile carbon.

Cycloaddition of Heterocummulenes with 1. The rich cycloaddition chemistry of **1** prompted study with heterocummulenes. Previous studies have focused on functionalization of activated group 4 transition metal dinitrogen compounds with heterocummulenes.[42,46] Less attention has been devoted to nitride functionalization following N_2 cleavage.

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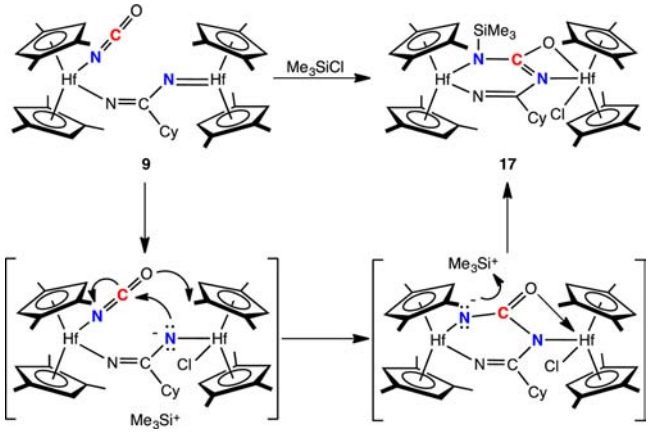
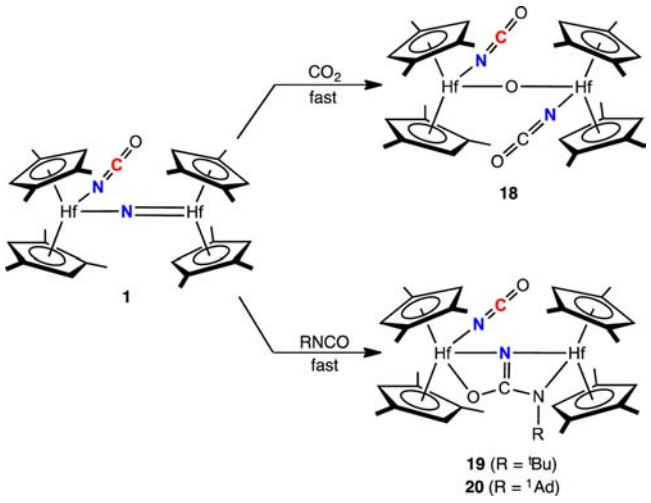
Scheme 6. Treatment of Dihafnocene Ureate-Type Complexes with Me_3SiCl



Addition of 1 equiv of CO_2 gas to a benzene-d_6 solution of **1** resulted in rapid precipitation of an off-white solid identified as the μ-oxo dihafnocene bis(isocyanate) complex, **18** (Scheme 7). The ^{1}H NMR spectrum established equivalent hafnocene

Scheme 7. Addition of Heterocummulenes to 1



subunits, while the presence of terminal isocyanate ligands was readily identified by IR and ^{13}C NMR spectroscopies. The solid state infrared spectrum in KBr exhibits two strong [NCO] bands at 2222 and 2085 cm^{-1}, which shift to 2160 and 2027 cm^{-1} upon labeling with ^{13}CO and $^{13}CO_2$ (harmonic oscillator: 2176 and 2041 cm^{-1}). The ^{13}C NMR spectrum of **18-^{13}C** exhibits a broad singlet centered at 135.3 ppm.

Formation of **18** likely proceeds by initial cycloaddition of CO_2 across the Hf–N bond to form a μ_2-$[NCO_2]^{3-}$ ligand, which undergoes rearrangement to form the observed μ-oxo core and a terminal isocyanate. Similar deoxygenation reactions have been observed with $(\eta^5\text{-}C_5H_5)_2ZrNR$ complexes upon addition of isocyanates.[47] In an attempt to suppress deoxygenation chemistry and observe heterocummulene cycloaddition to the dihafnocene imido, **1** was treated with alkyl isocyanates. Addition of 1 equiv of ^{t}BuNCO to a benzene-d_6 solution of **1** at 23 °C rapidly and cleanly furnished the desired cycloaddition product, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}NCON^tBu)(NCO)$ (**19**) in 75% yield following washing of the crude material with pentane at −35 °C (Scheme 7).

Like **4**, the benzene-d_6 ^{1}H NMR spectrum of **19** exhibits the number of resonances expected for a C_s symmetric compound but the ^{13}C NMR spectrum contains both an isocyanate resonance at 132.0 ppm and a new peak centered at 159.7 ppm. Preparation of the ^{15}N/^{13}C isotopologue from $^{15}N_2$ and ^{13}CO gas resulted in splitting of the broad singlet at 132.0 ppm into a doublet ($^1J_{CN}$ = 32.6 Hz). Unfortunately, no C–N coupling was observed for the resonance at 159.7 ppm but the ^{15}N NMR spectrum of **19** clearly exhibits a resonance at 90.2 ppm for a terminal isocyanate and a new resonance at 221.8 ppm, shifted significantly upfield from **1** (589.9 ppm) consistent with formation of a ureate ligand.

The solid-state structure of **19** was determined by X-ray diffraction and definitively confirmed formation of a ureate ligand from isocyanate cycloaddition (Figure 9). The core of

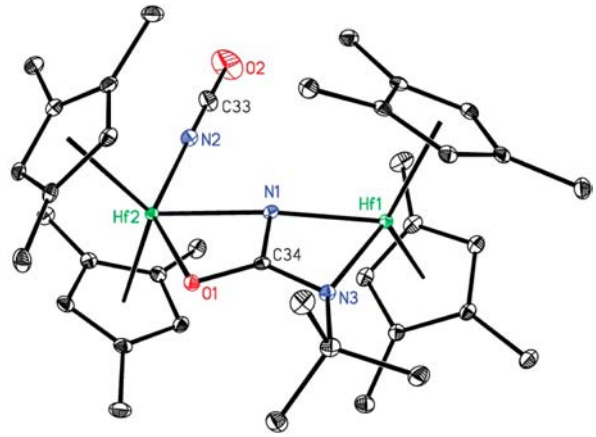


Figure 9. Molecular structure of **19** at 30% probability ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances (Å): Hf(1)–N(1) = 2.105(2), Hf(2)–N(1) = 2.231(2), Hf(1)–N(3) = 2.144(2), N(1)–C(34) = 1.360(3), and N(3)–C(34) = 1.361(3).

the ureate ligand features indistinguishable C(34)–N(1) and C(34)–N(3) bond lengths of 1.360(3) and 1.361(3) Å, while the C(34)–O(1) distance is significantly shorter with a value of 1.298(3) Å. Unlike zirconium imido compounds studied by Bergman, where cycloaddition of isocyanates leads to formation of $[Cp_2ZrO]_x$ and carbodiimides,[47] the second hafnium center in **19** likely stabilizes the resultant μ-ureate core and inhibits immediate deoxygenation. Similar cycloaddition reactivity was observed with 1-adamantyl isocyanate and yielded the analogous isocyanato dihafnocene ureate product, **20** in 87% yield following recrystallization (Scheme 7). The spectroscopic signatures of **20** are similar to **19** and the solid-state structure was also confirmed by X-ray diffraction and is presented in the SI. Attempts to prepare analogous products by cycloaddition of benzyl or *p*-tolyl isocyanate with **1** were unsuccessful, producing unidentified mixtures of organometallic products.

The observation of rapid formation of a μ-oxo hafnocene product following CO_2 cycloaddition prompted study of the thermal stability of **19** and **20**. Heating a benzene-d_6 solution of **19** to 110 °C and monitoring the progress of the reaction by NMR spectroscopy over the course of 18 h established gradual rearrangement to the μ-oxo dihafnocene carbodiimidyl complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(N{=}C{=}N^tBu)(\mu_2\text{-}O)$ (**21**) (Scheme 8). The ^{13}C NMR spectrum of **21-^{13}C,^{15}N** retained the resonance for the isocyanate carbon centered at 135.2 ppm while the carbodiimidyl resonance

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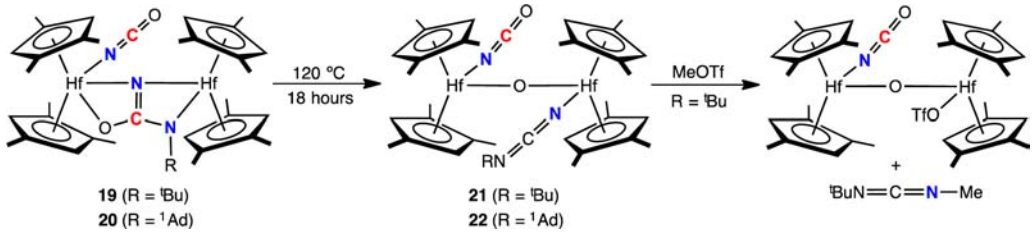
Scheme 8. Thermal Rearrangement of 19 and Carbodiimidyl Group Transfer



19 (R = ^{t}Bu)
20 (R = ^{1}Ad)
21 (R = ^{t}Bu)
22 (R = ^{1}Ad)

appeared as a doublet at 137.4 ppm ($^1J_{CN}$ = 29.9 Hz). The ^{15}N NMR spectrum of **21**-^{13}**C,**^{15}**N** contains the expected isocyanate doublet at 86.1 ppm ($^1J_{CN}$ = 33.1 Hz), as well as a new resonance at 143.7 ppm (see SI). The benzene-d_6 solution infrared spectrum of **21** exhibited a moderate intensity band at 2125 cm^{-1} for the terminal carbodiimidyl ligand and a stronger band at 2083 cm^{-1}, which shifted to 2007 cm^{-1} upon labeling with $^{15}N_2$ and ^{13}CO gas (2006 cm^{-1} expected for simple harmonic oscillator). Similar thermal isomerization was observed with the 1-adamantyl-substituted compound, **20** and the resulting μ-oxo dihafnocene complex, [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(N═C═N^{1}Ad)(μ_2-O) (**22**) exhibits similar spectroscopic features to **21**. This isomerization is likely driven by the formation of the μ-oxo bridge, allowing access to new nitrogen-containing ligands following N_2 cleavage.

To our knowledge, synthesis of a carbodiimidyl ligand following N_2 cleavage is unprecedented and accordingly, group transfer of the newly formed [RNCN] ligand was explored. Addition of methyl trifluoromethanesulfonate (MeOTf) to a benzene-d_6 solution of **21** resulted in complete conversion to the previously characterized dihafnocene complex, [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(OTf)(μ_2-O) (Scheme 8).[31] Vacuum transfer of the volatile components and analysis by ^{1}H NMR spectroscopy established formation of 1-*tert*-butyl-3-methyl-carbodiimide.

■ CONCLUSIONS

A base free dihafnocene nitride complex has been prepared from rapid CO-induced cleavage of molecular nitrogen at ambient temperature. The synthesis of this compound allowed exploration of the fundamental reactivity of this rare linkage. While metastable in solution, this molecule is a versatile platform for forming new nitrogen−carbon bonds to a μ-nitrido ligand formed from N_2 cleavage. Activated alkynes, organonitriles, and heterocummulenes, such as CO_2 and isocyanates, all promote N−C bond formation, each via a distinct pathway. In many cases, the terminal hafnium isocyanate ligand participates in additional N−C bond forming chemistry further expanding the number of available transformations for elaborating both dinitrogen and carbon monoxide following CO-induced N_2 cleavage. Perhaps most notably, the present studies establish new organometallic routes to nitrogen−carbon bond forming reactions available to bridging nitrides following N_2 splitting.

■ EXPERIMENTAL SECTION[48]

Spectroscopic Characterization of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-N) (1). A J. Young NMR tube was charged with 0.012 g (0.015 mmol) of [(η^5-$C_5Me_3H_2$)$_2$Hf]$_2$(η^2, η^2-N_2) and 0.45 g of benzene-d_6. The tube was removed from the glovebox and 1 equiv of CO gas was added at 77 K. The solution was thawed and shaken, and a clear red solution was observed. The resulting mixture was immediately analyzed by multinuclear NMR and IR spectroscopy. ^{1}H NMR (benzene-d_6, 23 °C): δ 2.13 (br s, 6H, C_5H_2-1,2,4-Me_3), 2.16 (br s, 6H, C_5H_2-1,2,4-Me_3), 2.31 (br s, 6H, C_5H_2-1,2,4-Me_3), 2.37 (br s, 6H, C_5H_2-1,2,4-Me_3), 2.46 (br s overlapping, 6H, C_5H_2-1,2,4-Me_3), 2.47 (br s overlapping, 6H, C_5H_2-1,2,4-Me_3), 5.55 (br s, 2H, C_5H_2-1,2,4-Me_3), 5.82 (br s, 2H, C_5H_2-1,2,4-Me_3), 6.11 (br s, 2H, C_5H_2-1,2,4-Me_3), 6.26 (br s, 2H, C_5H_2-1,2,4-Me_3). {^{1}H}^{13}C NMR (benzene-d_6, 23 °C): δ 131.0 (broad d, $^1J_{CN}$ = 35.4, NCO). {^{1}H}^{15}N NMR (benzene-d_6, 23 °C): δ 98.22 (d, $^1J_{CN}$ = 35.4, *N*CO), 589.86 (s, Hf-*N*-Hf). IR (KBr): 2221 cm^{-1} (NCO).

General Procedure for Functionalization Reactions. A Teflon capped NMR tube was charged with 0.500 g of a benzene solution containing 0.020 g (0.025 mmol) of [(η^5-$C_5Me_3H_2$)$_2$Hf]$_2$(η^2, η^2-N_2). One equivalent of carbon monoxide gas was added to the frozen and degassed solution on the high vacuum line. The contents of the tube were immediately degassed to remove any excess carbon monoxide. Functionalization with volatile reagents was accomplished by addition from a calibrated gas bulb on the vacuum line. Nonvolatile reagents were added via microsyringe after transferring the tube into a glovebox. A procedure and full characterization data for cyclooctyne addition to yield **3** is presented in detail below, all other compounds are reported in the SI.

Preparation of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2,k^2-N-(cyclooctenyl)) (3). A J. Young NMR tube was charged with 0.013 g (0.016 mmol) of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(μ_2,η^2,η^2-N_2) and 0.450 g of benzene. The solution was frozen at the high vacuum line, degassed, and approximately 1 equiv of CO was added at 77 K. The tube was thawed and shaken vigorously for 10 s, turning dark red. The tube was immediately degassed and brought into the glovebox, where 2.0 μL (0.016 mmol) of cyclooctyne was added via microsyringe. The reaction was left at room temperature for 2 h before the volatiles were removed in vacuo and the oily red residue washed with cold pentane (2 × 5 mL) to yield an analytically pure off-white powder (0.045 g, 0.069 mmol, 59% yield from 5 combined tubes). This reaction has proven difficult to scale due to sensitivity to the amount of added carbon monoxide. It has proven most convenient to repeat the procedure with the reported amounts rather than altering the scale of the procedure. Anal. Calcd for $C_{41}H_{56}Hf_2N_2O$: C, 51.84; H, 5.94; N, 2.95. Found: C, 51.45; H, 5.88; N, 2.40. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.68 (m overlapped, octyl CH_2), 1.71 (m overlapped, 2H, octyl CH_2), 1.80 (m overlapped, 2H, octyl CH_2), 1.84 (s, 6H, C_5H_2-1,2,4-Me_3), 1.89 (s, 6H, C_5H_2-1,2,4-Me_3), 1.89 (m overlapped, 2H, octyl CH_2), 1.99 (s, 6H, C_5H_2-1,2,4-Me_3), 2.16 (s, 6H, C_5H_2-1,2,4-Me_3), 2.21 (s, 6H, C_5H_2-1,2,4-Me_3), 2.36 (m overlapped, 2H, allylic CH_2), 2.53 (s, 6H, C_5H_2-1,2,4-Me_3), 3.03 (t, $^3J_{HH}$ = 6.0, 2H, allylic CH_2), 5.28 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.55 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.78 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.80 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3). {^{1}H}^{13}C NMR (benzene-d_6, 23 °C): δ 12.8, 13.7, 14.4, 14.5, 15.3, 16.3 (C_5H_2-1,2,4-Me_3), 24.7, 26.7, 28.6, 31.1, 31.6, 42.1 (octyl CH_2), 110.5, 113.4, 113.5, 113.9, 114.1, 115.5, 118.5, 121.6, 123.4, 123.8 (C_5H_2-1,2,4-Me_3), 133.2 (octenyl Hf-C), 135.9 (d, $^1J_{CN}$ = 31.9, NCO), 173.1 (octenyl N-C). ^{15}N NMR (benzene-d_6, 23 °C) δ 87.93 (d, $^1J_{CN}$ = 31.9, *N*CO), 286.58 (s, Hf-*N*-Hf). IR (benzene-d_6): ν_{NCO} = 2084 cm^{-1}, $\nu_{15N13CO}$ = 2022 cm^{-1}, ν_{CC} = 1994 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, including general considerations and spectroscopic details. Representative multinuclear NMR spectra and crystallographic data in cif format for **4**, **5**, **6**, **10**, **11**, **14**, **15**, **19**, and **20**. This material is available free of charge via Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(48) Representative procedures are described herein. General considerations and additional experimental procedures are reported in the Supporting Information.