ORGANOMETALLICS

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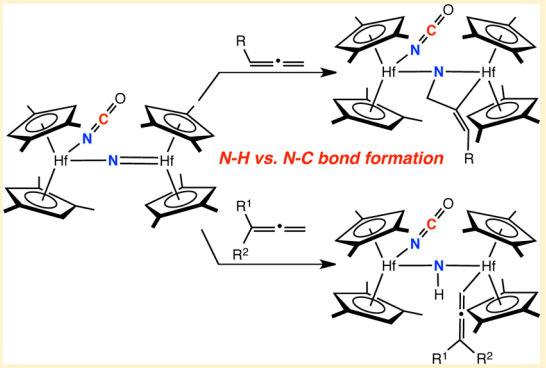
N–H and N–C Bond Formation with an N_2-Derived Dihafnium μ-Nitrido Complex

Scott P. Semproni and Paul J. Chirik*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

Supporting Information

ABSTRACT: Exposure of the base-free isocyanato dihafnocene μ-nitrido complex prepared from CO-induced N_2 cleavage to a dihydrogen atmosphere resulted in rapid 1,2-addition across the hafnium–nitrogen bond followed by insertion of the terminal isocyanate ligand into the putative hafnium hydride ligand and formed a bridging formamide ligand. Terminal alkynes and sterically hindered allenes underwent preferential addition of a C–H bond across the hafnium nitride fragment and resulted in isolation of the μ-imido acetylide and allenyl dihafnocene complexes, respectively. Reducing the steric profile of the allene enabled N–C rather than N–H bond-forming chemistry arising from cycloaddition of the π system. In the presence of additional allene, the resulting azahafnacyclobutanes underwent exchange, establishing the reversibility of the N–C bond forming reaction. Ketones with enolizable hydrogens, amines, and guanidines underwent rapid deprotonation upon addition to the isocyanato dihafnocene μ-nitrido complex and offer a route to N–H bond formation, as well as allowing isolation of a rare example of a parent amido compound. The preference of the dihafnium nitrido system for N–H over N–C bond formation was explored by treatment with styrene oxide, which afforded exclusively the E_2 elimination product rather than the expected 1,2-amino alkoxide complex.



INTRODUCTION

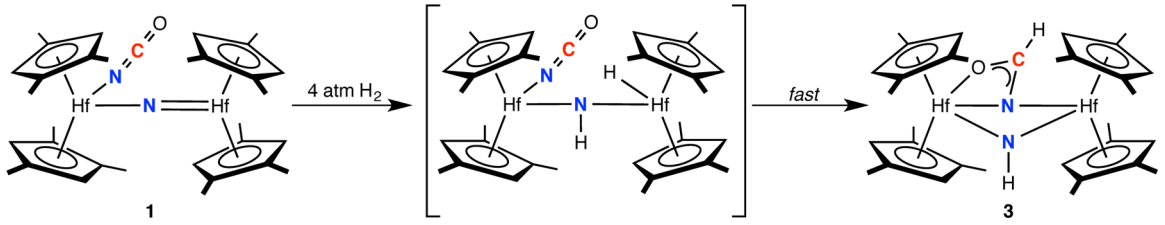
Dinitrogen cleavage by transition-metal compounds to the corresponding molecular nitrides has been a longstanding challenge in coordination and small-molecule activation chemistry.[1] Often N_2-derived metal nitrides have proven resistant to further functionalization, a result of favorable thermodynamics associated with the dinitrogen cleavage reaction.[2] Nevertheless, examples of acylation,[3] hydrogenation,[4] silylation,[5] and alkylation[6] reactions have been reported. Given the depth and breadth of reaction chemistry associated with group 4 imido complexes well-studied by Bergman,[7] Wolczanski,[8] and others,[9] we targeted the synthesis of bimetallic group 4 μ-nitrido complexes with the goal of imparting imido character into the metal–nitrogen linkage and providing new opportunities for elaboration of an N_2-derived molecular nitride.

Our laboratory has applied CO-induced N_2 bond cleavage, a process first described by Sobota and co-workers in titanium chemistry,[10] to the preparation of dizirconium and dihafnium oxamidide complexes.[11] Related chemistry by Fryzuk and co-workers on diamido bis(phosphine) complexes of tantalum[12] had previously demonstrated that various hydride reagents also induce N_2 bond cleavage,[13] although in many cases ligand degradation accompanied nitride functionalization.[14] Attempts to observe the putative μ-nitride intermediate with the original *ansa*-hafnocene that promotes CO-induced N_2 cleavage were unsuccessful due to rapid cyclometalation of the cyclopentadienyl substituents.[11a] Recently, we discovered that carbonylation of the less sterically encumbered hafnocene dinitrogen complex $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2\text{:}\eta^2\text{-}N_2)$ resulted in observation of the first dihafnium μ-nitride complex, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(\mu_2\text{-}N)$ (**1**).[15] Structural characterization was achieved by addition of 4-OMe-pyridine, and the solid-state structure of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(\mu_2\text{-}N)(4\text{-}OMe\text{-}pyridine)$ (**2**) exhibits features that suggested additional functionalization chemistry by cycloaddition or nucleophilic pathways should be possible. DFT studies also corroborated this view. Indeed, addition of sufficiently activated alkynes or heterocumulenes resulted in cycloaddition chemistry,[16] while treatment of **1** with alkyl triflates or halosilanes demonstrated the nucleophilicity of the μ-nitride.[17] Given the established ability of group 4 transition-metal imides and dinitrogen complexes to undergo 1,2-addition reactions with nonpolar substrates such as dihydrogen[8c] and even unactivated C–H bonds,[8,18] we sought to extend this reactivity to the μ-nitride fragment in **1** as a means to couple additional nitrogen–element bond formation with N_2 cleavage. Here we describe the hydrogenation, C–H addition of terminal alkynes and allenes, deprotonation chemistry of carbonyl compounds, and allene cycloaddition as means to form N–H and N–C bonds from **1**.

Received: April 14, 2014
Published: July 7, 2014

   dx.doi.org/10.1021/om500393n | *Organometallics* 2014, 33, 3727–3737

Scheme 1. 1,2-Addition of Dihydrogen to 1



RESULTS AND DISCUSSION

Hydrogenation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(\mu_2\text{-}N)$ (1). Our studies commenced with the hydrogenation chemistry of **1** and was inspired by the 1,2-addition chemistry known for zirconocene imido complexes.[19] Exposure of a benzene-d_6 solution of **1** to 4 atm of H_2 gas for 1 h resulted in quantitative formation of a new C_s-symmetric compound identified as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}NH)(\mu_2\text{-}NC(H)O)$ (**3**), arising from initial 1,2-addition of H_2 across the Hf−N bond followed by isocyanate insertion into the bridging metal hydride (Scheme 1). We believe the proximity of the two hafnocenes, enabled by the relatively sterically unencumbered cyclopentadienyl ligands, promotes the insertion of the isocyanate into the distal hafnocene hydride.[16,17] In all cases involving the generation of **1**, the reactions were most conveniently conducted on NMR tube scales due to the sensitivity of the reaction to the pressure and stoichiometry of CO and to avoid formation of hafnocene oxamidide products.[20]

The benzene-d_6 ^{1}H NMR spectrum of **3** contains a number of broad cyclopentadienyl resonances as well as two broad singlets at 4.11 and 9.60 ppm corresponding to the NH and NCHO protons, respectively. These assignments were confirmed by the preparation of the ^{15}N,^{13}C isotopologue $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}^{15}NH)(\mu_2\text{-}^{15}N^{13}C(H)O)$ (**3-^{15}N, ^{13}C**), which splits the 4.11 ppm signal into a doublet ($^1J_{NH}$ = 61.8 Hz) and the 9.60 ppm signal into a doublet of doublets ($^1J_{CH}$ = 187.6 Hz, $^2J_{NH}$ = 9.4 Hz). The formamidide carbon was observed by ^{13}C NMR spectroscopy as a broad, isotopically enhanced signal at 171.2 ppm, while the μ-imido nitrogen was located in the ^{15}N NMR spectrum as a doublet at 248.5 ppm. Single-crystal X-ray diffraction on colorless crystals of **3** obtained from cooling a concentrated fluorobenzene/pentane solution of the compound to −35 °C confirmed the identity of the product (Figure 1). The C−N and C−O bond lengths of 1.274(8) and 1.300(8) Å in the μ-formamidide ligand are indicative of delocalization of electron density among all three atoms. The proximity of the other hafnium to the site of 1,2-addition provides an additional reaction pathway not available to more sterically encumbered metallocene complexes which undergo similar 1,2-addition reactions.[11a] Protonation of **3** in benzene-d_6 solution with excess gaseous HCl provided formamide and ammonium chloride, as determined by ^{1}H NMR spectroscopy.

C−H Bond Addition of Terminal Acetylenes. The observed 1,2-addition and subsequent isocyanate hydride insertion chemistry observed upon hydrogenation of **1** promoted the exploration of other substrates that may undergo cycloaddition with the μ-nitrido dihafnium core. Previously, we reported that the activated, strained alkyne cyclooctyne underwent cycloaddition upon addition to **1**, resulting in formation of a metastable but crystallographically characterized azohafnocyclobutene.[16] Inspired by precedent established by

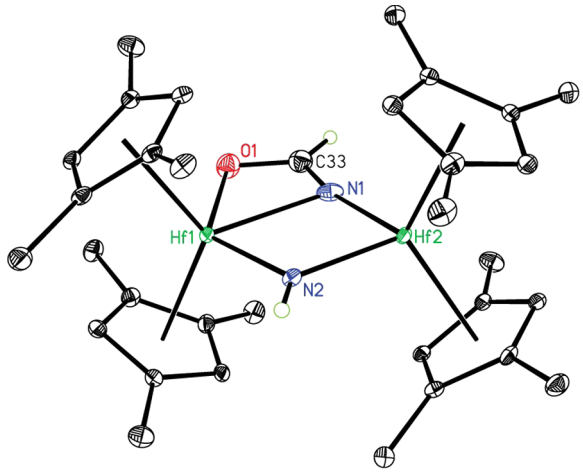


Figure 1. Representation of the molecular structure of **3** with 30% probability ellipsoids. Fluorobenzene solvate and hydrogen atoms (except those attached to N2 and C33) are omitted for clarity.

Fryzuk,[21] who demonstrated N−C bond formation from addition of terminal aryl acetylenes to a bis(phosphine)diamido zirconium complex with a strongly activated dinitrogen ligand, the reactivity of **1** and terminal alkynes was investigated. Addition of 1 equiv of phenylacetylene to a benzene-d_6 solution of **1** resulted in immediate consumption of starting material with concomitant formation of a new, C_s-symmetric hafnocene compound. Analysis of the reaction mixture by ^{1}H NMR spectroscopy and associated ^{1}H−^{13}C HSQC experiments revealed a broad signal at 7.01 ppm corresponding to a single proton that is not attached to a carbon atom. Preparation of the ^{15}N/^{13}C isotopologue resulted in the splitting of this signal into a doublet, confirming N−H bond formation, though accurate measurement of the ^{15}N−^{1}H coupling constant ($^1J_{NH}$ = 46.4 Hz) was complicated by poor resolution from overlap with aryl resonances and ultimately had to be determined from the ^{15}N NMR spectrum. The benzene-d_6 ^{15}N NMR spectrum revealed the expected terminal isocyanate resonance as a doublet at 91.7 ppm ($^1J_{CN}$ = 32.6 Hz), as well as an additional doublet at 283.4 ppm ($^1J_{NH}$ = 46.4 Hz). These data, coupled with solution IR bands at 3575 cm^{-1} (ν_{NH}) and 2038 cm^{-1} (ν_{CC}) confirmed the identity of the new product as the μ-imido acetylide complex $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(CCPh)(\mu_2\text{-}NH)$ (**4**), arising from 1,2-addition of the acetylene C−H bond across the metal−imido linkage instead of cycloaddition. Complex **4** was more conveniently prepared on a preparative scale from the reaction of the pyridine-stabilized nitride **2** with phenylacetylene at 75 °C for 18 h. The higher temperature required highlights the increased reactivity of the base-free complex. In an attempt to bias the reaction outcome toward cycloaddition, the base-free complex **1** was treated with trimethylsilylacetylene, but this resulted in 1,2-addition of the acetylene C−H

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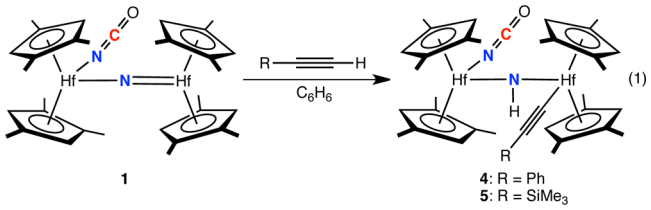
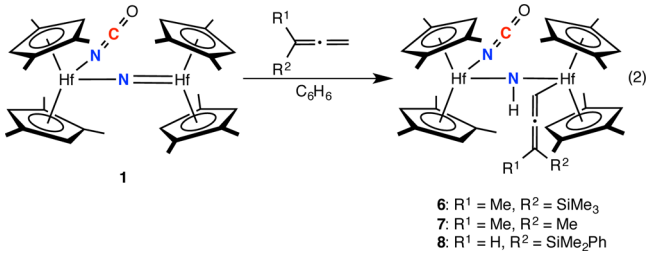
bond to form the imido-acetylide complex **5** (eq 1), which exhibited spectroscopic features similar to those of **4** (see the



Supporting Information). This reactivity parallels observations reported by Bergman and co-workers, where 1,2-addition of phenyl- and trimethylsilylacetylene to a titanocene imido complex was observed.[22] Similar 1,2-addition chemistry was observed upon treatment of zirconocene dinitrogen complexes with terminal acetylenes to afford diazenido bis(acetylide) complexes.[23]

Vinylic C−H Bond Addition of Sterically Hindered Allenes. The divergent reactivity between acetylene 1,2-addition to form N−H bonds versus cycloaddition to assemble N−C bonds prompted us to explore the chemistry of **1** with other activated π systems. Allenes were attractive, given their commercial availability, modularity, and established rich reaction chemistry with other early-metal imido compounds.[24,25] Addition of 1 equiv of commercially available 1-methyl-1-trimethylsilylallene to a benzene-d_6 solution of **1** resulted in the immediate consumption of starting material and the formation of a new hafnocene product identified as **6** (eq 2).



The benzene-d_6 ^{1}H NMR spectrum of **6** exhibited a quartet at 5.07 ppm corresponding to a single proton, which was assigned to the vinyl C−H on the basis of ^{1}H−^{13}C HSQC experiments. A broad singlet at 6.43 ppm also corresponding to a single proton was also observed, which split into a doublet ($^1J_{NH}$ = 45.6 Hz) upon preparation of the ^{15}N/^{13}C isotopologue. The benzene-d_6 ^{15}N NMR spectrum of **6** exhibited two doublets at 91.5 ($^1J_{CN}$ = 33.3 Hz) and 279.9 ppm ($^1J_{NH}$ = 45.6 Hz) corresponding to terminal isocyanate and μ-imido ligands, respectively (see the Supporting Information). Two-dimensional NMR experiments with **6** proved particularly useful for determining the fate of the allene. A methine resonance centered at 69.8 ppm is coupled to the vinylic proton at 5.07 ppm in the ^{1}H NMR spectrum, confirming C−H addition from the terminal position of the allene ligand. The other allene carbon resonances were located at 110.3 and 208.6 ppm for the disubstituted and internal carbons, respectively.

A single-crystal X-ray diffraction experiment confirmed the identity of **6** as the μ-imido allenyl hafnocene complex arising from addition of a vinylic C−H bond across the Hf═N unit (Figure 2). Inspection of the metrical parameters revealed retention of both allenic double bonds with a C(34)−C(35)−C(36) bond angle of 176.9(6)° and C(34)−C(35) and C(35)−C(36) bond distances of 1.293(4) and 1.318(8) Å, respectively. Previously Bergman and co-workers reported that zirconocene imido complexes undergo cycloaddition of various 1,3-disubstituted allenes.[24c] To our knowledge, the vinylic C−H addition of these substrates by 1,2-addition to a μ-nitride as observed with **1** represents a new reactivity mode for these compounds.

To determine whether the bulky trimethylsilyl substituent on the allene was inhibiting cycloaddition and was ultimately the origin of the observed C−H addition chemistry, the μ-nitrido hafnocene was treated with smaller allenes with the goal of accessing the π system and enabling N−C bond formation. Addition of 1,1-dimethylallene to a benzene-d_6 solution of **1** followed by recrystallization from a pentane−fluorobenzene mixture yielded colorless crystals identified as the μ-imido allenyl hafnocene complex **7** in 75% yield (eq 2). Complex **7** exhibited spectroscopic features very similar to those of **6**, including a broad singlet at 6.28 ppm in the benzene-d_6 ^{1}H NMR spectrum, diagnostic for the N−*H* of the μ-imido ligand. Solid-state IR data (KBr pellet) revealed an N−H stretching

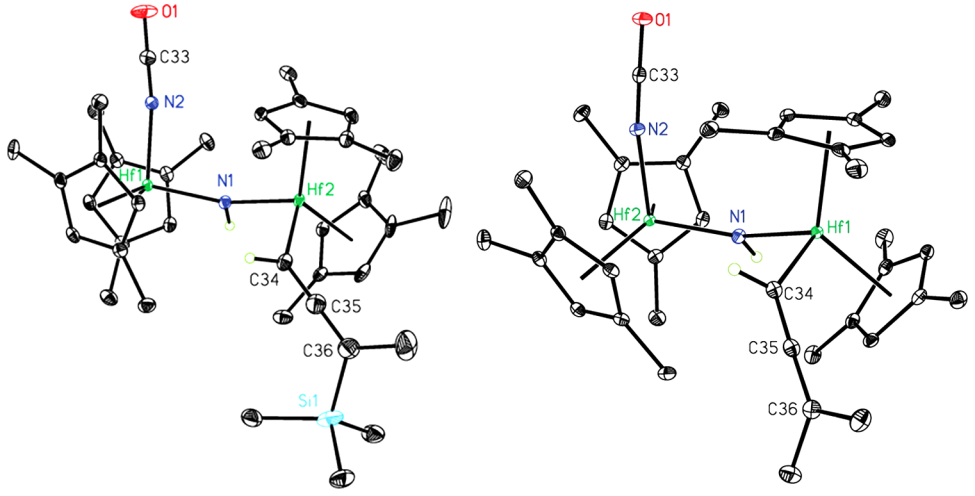


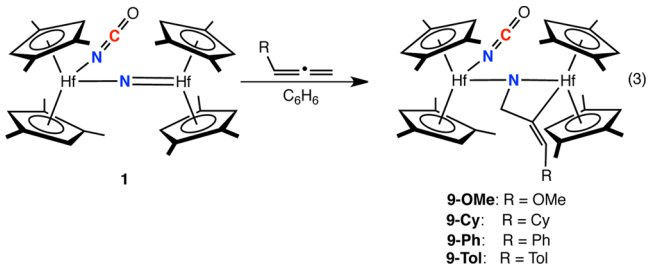
Figure 2. Representations of the molecular structures of **6** (left) and **7** (right) with 30% probability ellipsoids. One molecule of fluorobenzene solvate and hydrogen atoms (except those attached to N1 and C34) are omitted for clarity.

dx.doi.org/10.1021/om500393n | *Organometallics* 2014, 33, 3727−3737

mode at 3566 cm^{-1} as well as an allenyl C═C stretch at 1922 cm^{-1}, in addition to the bands typically observed for the terminal isocyanate ligand.[11] A single-crystal X-ray diffraction experiment confirmed addition of one of the terminal C−H bonds of the dimethylallene ligand (Figure 2). The reversibility of the C−H addition reaction was probed by heating a benzene-d_6 solution of either **6** or **7** to 80 °C for 18 h in the presence of excess PhCCH. No change was observed, demonstrating that C−H addition via 1,2-elimination was not accessible under these conditions.

The observation of 1,2-addition with both 1-methyl-1-trimethylsilylallene and 1,1-dimethylallene suggested that geminal disubstitution may be preventing cycloaddition chemistry. Treatment of a benzene solution of **1** with 1-dimethylphenylsilylallene also yielded the C−H addition product $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(Me_2PhSiCH{=}C{=}CH)(\mu_2\text{-}NH)$ (**8**) in 60% isolated yield (eq 2). The identity of the product was established by multinuclear NMR spectroscopy, combustion analysis, and single-crystal X-ray diffraction (see the Supporting Information), which revealed the expected dihafnocene μ-imido core. Presumably cycloaddition of one of the allene C−C bonds is inhibited by the bulky $SiMe_2Ph$ group, which cannot be accommodated in the metallocene wedge.

Cycloaddition of Monosubstituted Allenes with 1. A series of monosubstituted allenes with substituents smaller than [$SiMe_2Ph$] were explored with the goal of encouraging cycloaddition chemistry and N−C bond formation. Treatment of a benzene solution of **1** with 1-methoxyallene produced the new C_s-symmetric dihafnocene complex **9-OMe** in 66% isolated yield (eq 3).



(3)

The ^1H and ^{13}C NMR spectra of **9-OMe** exhibited features that ultimately proved diagnostic for the cycloaddition product. The methylene unit adjacent to the μ-imido nitrogen appeared as a doublet at 3.36 ppm corresponding to two protons in the ^1H NMR spectrum and engaged in long-range coupling to the vinylic proton of the allene unit ($^4J_{HH}$ = 2.8 Hz) located at 5.78 ppm. No N−H resonances were observed by ^1H NMR or IR spectroscopy. The $\{^1H\}^{13}C$ NMR spectrum of **9-OMe** revealed a resonance attributable to the methylene carbon of the former allene at 39.3 ppm, shifted more than 30 ppm upfield from the C−H activated carbon in **6** (69.8 ppm). The ^{15}N NMR spectrum of **9-OMe-^{15}N/^{13}C** in benzene-d_6 displayed the expected doublet at 86.8 ppm ($^1J_{CN}$ = 31.9 Hz) consistent with the terminal isocyanate ligand, as a well as a signal at 269.0 ppm, which did not exhibit any N−H coupling.

The solid-state structure of **9-OMe** was determined by X-ray diffraction (Figure 3) and confirms cycloaddition of the terminal C═C bond of the methoxyallene substrate. Typical bent-metallocene coordination geometries are observed with Hf(1)−N(1) and Hf(2)−N(1) bond lengths of 2.099(3) and 2.052(3) Å, respectively, and the former allene substituent in

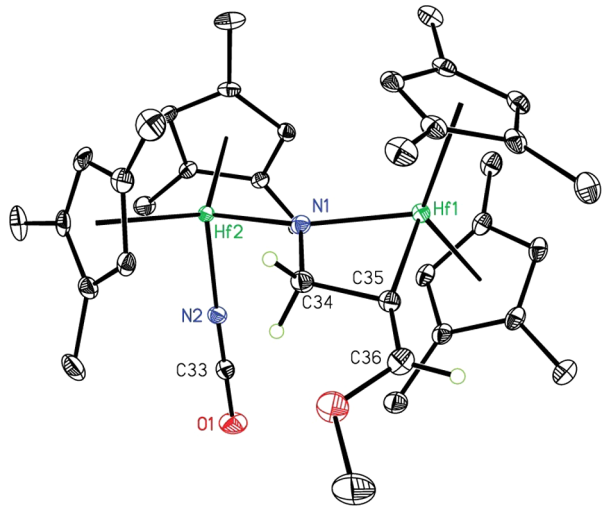


Figure 3. Representation of the solid-state structure of **9-OMe** with 30% probability ellipsoids. For one of the cyclopentadienyl rings, only one of the two possible orientations is shown. One molecule of disordered fluorobenzene solvate and hydrogen atoms (except those attached to C34 and C36) are omitted for clarity.

the configuration directed away from the hafnocene wedge. The C(34)−N(1) distance of 1.512(4) Å is consistent with a C−N single bond and unambiguously confirms N−C bond formation between the N_2-derived nitride and the allene substrate. The C(34)−C(35) bond of the former allene unit has lengthened to 1.553(5) Å upon cycloaddition, while C(35)−C(36) exhibits a characteristic double-bond length of 1.318(5) Å. The C(36)−C(35)−C(34) angle of 117.8(3)° is also consistent with cycloaddition, with the former central carbon of the allene substrate displaying a short Hf(1)−C(35) bond distance of 2.148(3) Å.

Unlike the product of cyclooctyne cycloaddition,[16] the azahafnacyclobutane subunit in **9-OMe** proved thermally stable upon heating to 80 °C for extended periods in benzene-d_6. No deoxygenation of the terminal isocyanate ligand was observed, and no evidence for retrocycloaddition and subsequent C−H addition of the terminal allene C−H bonds was obtained by ^1H NMR spectroscopy. The improved stability of the allene cycloaddition product toward isocyanate deoxygenation may be a result of reduced ring strain in the azahafnacyclobutane in comparison to the azahafnacyclobutene (Scheme 2). Attempting to leverage the inherent ring strain in the azahafnacyclobutane to enable additional dinitrogen functionalization[26] was unsuccessful, as treatment of **9-OMe** with H_2, CO, and organosilanes produced no reaction at room temperature and decomposition at elevated temperatures.

The scope of the cycloaddition and N−C bond forming reaction was investigated with other monosubstituted allenes. Treatment of benzene-d_6 solutions of **1** with 1-cyclohexylallene, 1-phenylallene, and 1-*p*-tolylallene yielded the desired cycloaddition products **9-Cy**, **9-Ph**, and **9-Tol** in 80%, 83%, and 58% yields, respectively, following recrystallization (eq 3). The new C_s-symmetric hafnocene products were characterized by a combination of multinuclear NMR spectroscopy, IR spectroscopy, combustion analysis, and (in the case of **9-Tol**) single-crystal X-ray diffraction (Figure 4). The relevant NMR spectroscopic parameters for **9-Cy** and **9-Ph** are reported in Table 1. In all cases, no evidence of C−H addition of the

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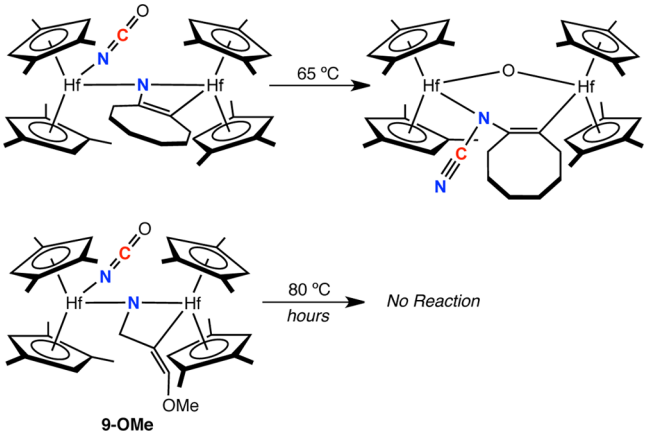
Scheme 2. Thermal Stability of Cyclooctyne and Methoxyallene Cycloaddition Products



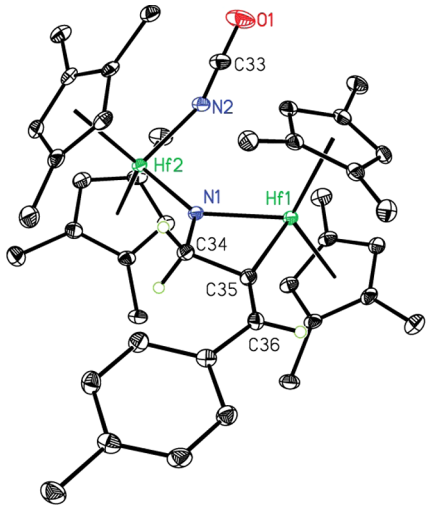


Figure 4. Representation of the molecular structure of **9-Tol** with 30% probability ellipsoids. One molecule of disordered fluorobenzene solvate and hydrogen atoms (except those attached to C34 and C36) are omitted for clarity.

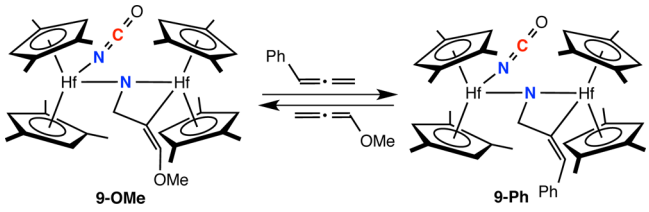
terminal CH_2 unit of the allene was observed at ambient temperature or upon heating to 80 °C.

Table 1. Summary of Multinuclear NMR Spectroscopic Data for 9-Cy and 9-Ph

compound	NCO ^{15}N shift (ppm)	NCO $^{1}J_{CN}$ (Hz)	imide ^{15}N shift (ppm)	N−CH_2 ^{1}H shift (ppm)	N−CH_2 ^{13}C shift (ppm)
9-Cy	86.1	32.4	269.7	3.11	40.1
9-Ph	87.4	32.1	267.9	3.57	43.0

The possibility of reversible allene cycloaddition was probed by treatment of a sample of **9-OMe** with 1 equiv of 1-phenylallene at room temperature in benzene-d_6. After 8 h, both **9-OMe** and **9-Ph** were present in an approximately 1:1 ratio as judged by NMR spectroscopy, demonstrating that retrocycloaddition and readdition of another substrate to these azahafnacyclobutanes is possible (Scheme 3). Heating the solution containing both hafnocenes to 65 °C for 18 h produced no change in the product ratio, while extended

Scheme 3. Reversibility of Allene Cycloaddition



heating at 110 °C resulted in decomposition to a mixture of unidentified products.

Attempts to extend the cycloaddition reactivity observed with monosubstituted allenes to 1,3-disubstituted alkylallenes have proven unsuccessful, as treatment of **1** with 1,2-nonadiene or 1,3-dimethylallene produced no reaction at room temperature, likely a result of steric destabilization of the requisite four-membered transition states required for 1,2- or cycloaddition. Likewise, the dihafnocene dinitrogen compound $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$ did not engage in productive N−H or N−C bond forming chemistry with various allenes. Upon treatment with methoxyallene or cyclohexylallene, decomposition to multiple unidentified products was observed, while treatment with 1,1-dimethylallene, 1,2-cyclononadiene, or 1-methyl-1-trimethylsilylallene produced no reaction at room temperature and decomposition upon mild thermolysis. Bergman and co-workers have reported the catalytic hydroamination of allenes using an imido titanium complex and postulated allene cycloaddition as a key N−C bond forming step.[27] These results highlight the unique ability of CO-induced N_2 cleavage to generate a μ-nitrido hafnocene to undergo productive N−H and N−C bond forming chemistry only available once the N−N bond is ruptured.

Addition of Ketones to 1: Deprotonation of Carbon Acids as a Route to N−H Bonds. Addition of carbonyl-containing substrates to **1** was of interest to determine if Hf−O bond formation was a sufficient driving force to enable the synthesis of various new azametallacycles arising from N−C bond formation. Bergman and co-workers reported that addition of various ketones to zirconocene imido complexes produced imines and polymeric zirconocene oxide when small ketones were used and produced amido enolate species arising from ketone deprotonation when the carbonyl substrate possessed at least one bulky substituent.[28] Our laboratory has demonstrated N−C bond formation by addition of alkyl and aryl isocyanates to hafnocene complexes bearing strongly activated dinitrogen ligands.[29]

Treatment of a benzene-d_6 solution of **1** with 1 equiv of 3,3-dimethyl-2-butanone at ambient temperature resulted in immediate consumption of the starting material with concomitant formation of a new C_s-symmetric dihafnocene product, **10**. The same product was obtained from treatment of the base-stabilized nitride **2** with 3,3-dimethyl-2-butanone. The latter reaction required 18 h at ambient temperature to reach completion. Analysis of the ^{1}H NMR spectrum of **10** revealed that the acyl methyl group was no longer present and was replaced by two singlets, each corresponding to a single proton, observed at 3.66 and 4.24 ppm. In addition, a broad singlet was observed at 6.56 ppm, which split into a doublet ($^{1}J_{NH}$ = 45.8 Hz) upon preparation of the ^{15}N/^{13}C isotopologue. Additionally, the solution IR spectrum recorded in benzene revealed a N−H stretch at 3472 cm^{-1} as well as a strong stretch at 1707 cm^{-1} in conjunction with the resonances expected for a

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terminal isocyanate ligand. These data, along with those from with a single-crystal X-ray diffraction experiment (Figure 5),

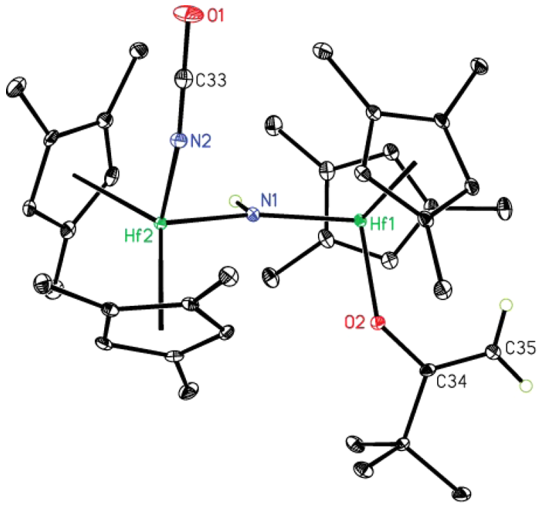
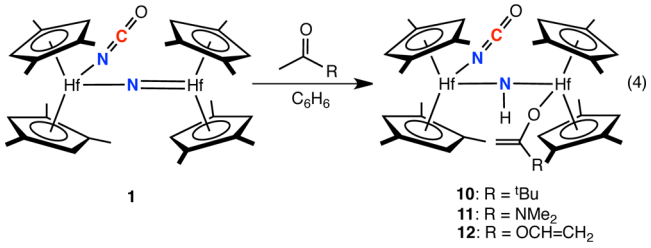


Figure 5. Representation of the molecular structure of **10** with 30% probability ellipsoids. Hydrogen atoms, except those attached to N1 and C35, are omitted for clarity.

support the formulation of **10** as the μ-imido dihafnocene enolate complex, arising from deprotonation of the α-methyl group by the basic μ-nitrido hafnocene fragment (eq 4).



1

10: R = ^{t}Bu
11: R = NMe_2
12: R = $OCH{=}CH_2$

Deprotonation of pinacolone by poryphrin-based zirconium and hafnium imido complexes to yield enolate amide species has been previously reported by Woo and co-workers,[9b] as well in zirconocene imido systems by Bergman and co-workers.[7b,28] In the porphyrin-based systems, however, addition of another 1 equiv of ketone leads to C−C coupling of the two carbonyl fragments.

The solid-state metrical parameters for compound **10** clearly indicate that deprotonation has occurred at the α-methyl group. An O(2)−C(34) bond length of 1.363(4) Å is consistent with carbon−oxygen single-bond character, while the C(34)−C(35) bond distance of 1.332(5) Å demonstrates significant enolate character in the bound pinacolone ligand. The hydrogen atom on N(1) was located in the difference map and freely refined. The ^{15}N NMR spectrum of **10**-^{15}**N**/^{13}**C** recorded in benzene-d_6 (Figure 6) exhibited the expected terminal isocyanate resonance as a doublet centered at 88.7 ppm ($^1J_{CN}$ = 32.4 Hz) in addition to a doublet centered at 258.3 ppm ($^1J_{NH}$ = 45.8 Hz) assigned as the μ-imido nitrogen, confirming retention of the solid-state structure in solution.

The generality of N−H bond formation by deprotonation of a carbon acid with **1** was probed with a number of other readily available carbonyl substrates. Treatment of a benzene solution of **1** with dimethylacetamide or vinyl acetate yielded, after workup and recrystallization, the μ-imido enolate products **11** and **12** in 70 and 80% yields, respectively (eq 4). Both C_s-symmetric dihafnocene products were characterized by multinuclear NMR and IR spectroscopy and (in the case of **11**) by single crystal X-ray diffraction (Figure 7). The ^{1}H NMR spectrum of each compound exhibited diagnostic vinyl CH resonances which signaled deprotonation of an α-methyl group in addition to broad singlet resonances corresponding to the proton on the newly formed μ-imido fragment.

Substrates lacking enolizable hydrogens were explored with the goal of encouraging N−C bond formation by cycloaddition of the π system. Addition of diphenylketene, benzaldehyde, benzophenone, and pivaldehyde to benzene-d_6 solutions of **1**

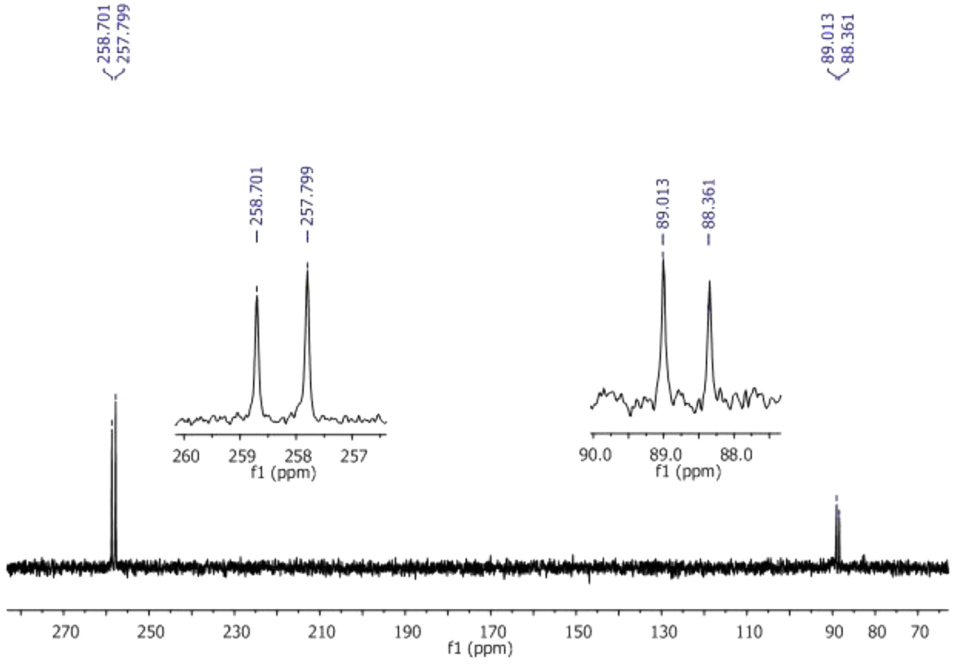


Figure 6. ^{15}N NMR spectrum of **10**-^{15}**N**/^{13}**C** in benzene-d_6 at 23 °C.

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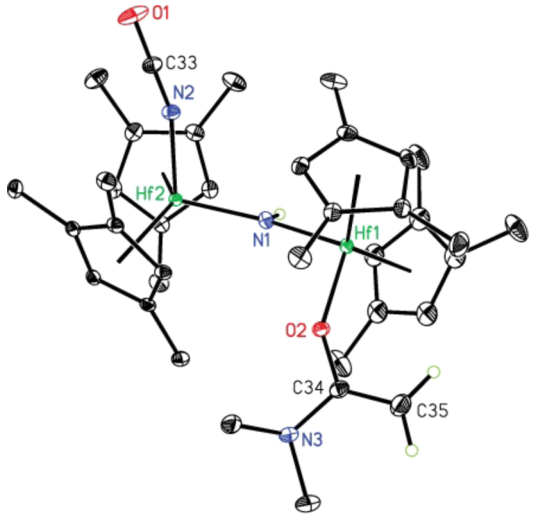
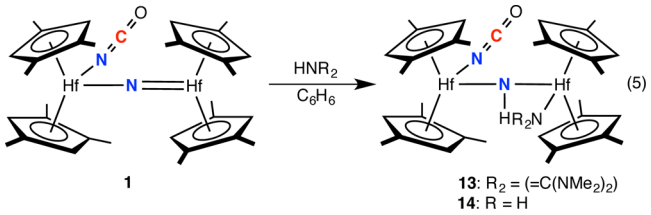


Figure 7. Representation of the molecular structure of **11** with 30% probability ellipsoids. Hydrogen atoms, except those attached to N1 and C35, and one molecule of tetrahydrofuran solvate are omitted for clarity. Only one of the two cyclopentadienyl methyl group orientations is shown.

produced mixtures of unidentified products. In contrast, treatment of **1** with 1,1,3,3-tetramethylguanidine in benzene-d_6 resulted in rapid consumption of the starting materials and appearance of a new C_s-symmetric hafnocene product, **13**, as judged by ^{1}H NMR spectroscopy. A broad resonance was observed at 6.98 ppm, which did not couple to any carbon atoms as determined by ^{1}H−^{13}C HSQC and HMBC NMR experiments. To ascertain whether cycloaddition or deprotonation of the guanidine substrate had occurred, the ^{15}N/^{13}C isotopologue was synthesized; analysis of **13**-^{15}**N**/^{13}**C** by ^{1}H NMR spectroscopy revealed that the singlet at 6.98 ppm had split into a doublet with $^1J_{NH}$ = 42.9 Hz, indicating that deprotonation of the guanidine substrate had occurred to



produce a μ-imido hafnocene guanidide complex (eq 5). The ^{15}N NMR spectrum of **13**-^{15}**N**/^{13}**C** in benzene-d_6 displayed a doublet at 261.0 ppm ($^1J_{NH}$ = 42.9 Hz) for the μ-imido ligand as well as the expected doublet at 84.2 ppm for the terminal isocyanate ligand. Compound **13** was also conveniently obtained from **2** on a preparative scale; however, this reaction requires hours to reach completion instead of seconds at room temperature, suggesting that pyridine dissociation and guanidine coordination must precede N−H bond formation.

To evaluate whether the nitrido ligand was directly deprotonating the guanidine and other carbonyl substrates or if precoordination was necessary, **1** was treated with the weak carbon acids fluorene and cyclopentadiene. No reaction occurred in either case at room or elevated temperatures, suggesting that initial substrate precoordination is necessary for deprotonation to occur.[30]

The possible intermediacy of group 4 metallocene imido, amido, and hydrazido compounds in N_2 hydrogenation[31] prompted exploration of the synthesis of hafnocene complexes with imido/parent amido ligands. Typically with modestly activated metallocene dinitrogen complexes such as $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$,[31e] addition of strong L-type donors causes N_2 dissociation and decomposition of the resulting organometallic.[29] When CO-induced N_2 cleavage is performed first, ligand loss is eliminated as a viable decomposition pathway. Thus, treatment of a benzene-d_6 solution of **1** with 1.5 equiv of ammonia at room temperature immediately yielded the new imido/amido dihafnocene complex **14**. Performing the reaction with a slight excess (1.5 equiv) of ammonia and the pyridine-stabilized dihafnium nitride **2** also produced **14** after 1 h at room temperature, unsurprising given the superior donor ability of ammonia in comparison to 1,1,3,3-tetramethylguanidine (vide supra). The ^{1}H NMR spectrum of **14** displays a broad singlet at 3.12 ppm, which corresponds to two protons and does not split into a doublet upon preparation of the ^{15}N/^{13}C isotopologue, resulting in its assignment as an ammonia-derived parent amido ligand. In contrast, the broad singlet at 5.39 ppm integrates to a single proton and splits into a doublet upon ^{15}N labeling ($^1J_{NH}$ = 45.8 Hz), clearly indicating the dinitrogen parentage of the μ-imido ligand. The ^{15}N NMR spectrum exhibited the expected resonances for a μ-imido amido hafnocene complex with only the isotopically enhanced imido and isocyanate resonances being observed (see the Supporting Information).

The solid-state structure of **14** was also determined by single-crystal X-ray diffraction and represents a rare example of a group 4 metallocene parent amido complex (Figure 8).[32] All of

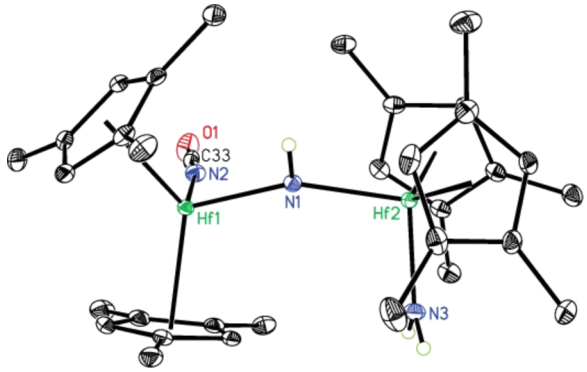


Figure 8. Representation of the molecular structure of **14** with 30% probability ellipsoids. Hydrogen atoms, except those attached to N1 and N3, are omitted for clarity.

the hydrogen atoms attached to nitrogen were located in the difference map and freely refined. Inspection of the metrical parameters revealed a short Hf(1)−N(1) bond length of 2.0373(18) Å, with a slightly longer Hf(2)−N(1) bond of 2.1210(18) Å. The parent amido−hafnium bond of Hf(2)−N(3) is similarly contracted at 2.041(2) Å, and the sum of angles around N(3) is 360.0°, consistent with the [−NH_2] formulation. It is well known that coordination of an amine to an electrophilic early transition metal center can have a dramatic effect on the value of the pK_a of the N−H bond in the resulting adduct.[33] Coordination of ammonia to the Lewis acidic Hf(IV) center in **1** likely facilitates proton transfer to the μ-nitrido ligand.

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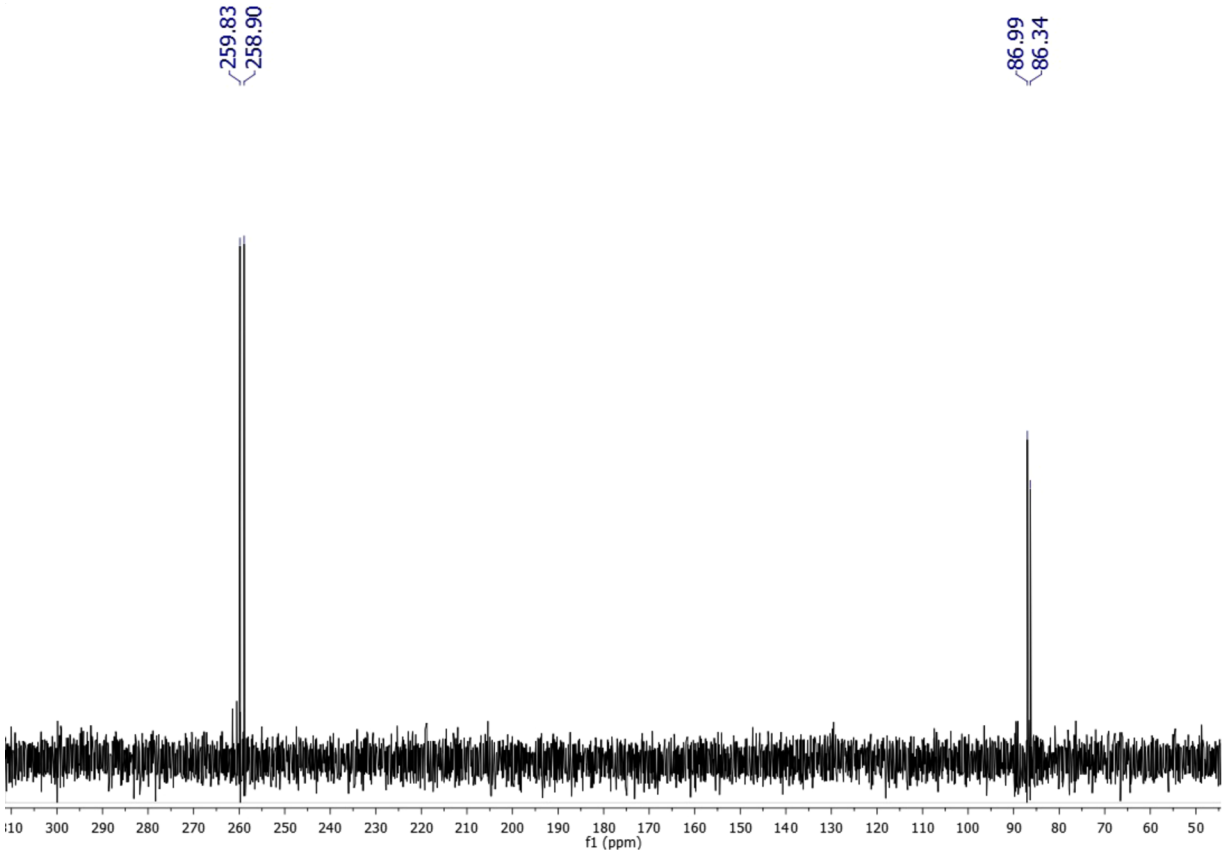
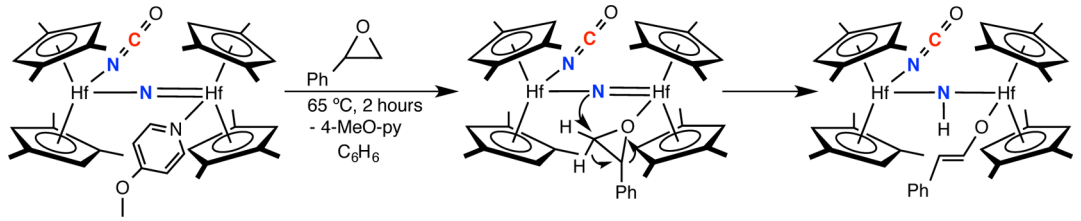


Figure 9. ^{15}N NMR spectrum of **15**-^{15}**N**,^{13}**C** in benzene-d_6 at 23 °C.

Scheme 4. Mechanism for E_2 Elimination of Hafnium-Bound Styrene Oxide



Given the facile deprotonation chemistry observed with **1** and mildly acidic C−H and N−H bonds, which in turn inhibits N−C bond forming chemistry, we turned our attention to epoxides. This class of substrates has been shown to undergo ring opening and N−C bond formation on addition to a zirconocene *tert*-butylimido complex, and subsequent protonolysis of the resulting zirconacycle afforded 1,2-diamino alcohols.[34] The synthesis of such compounds directly from N_2 is of interest, given the ease with which isotopic labels can be introduced into the resulting organic products. Treatment of **1** with 1 equiv of styrene oxide in benzene-d_6 resulted in immediate consumption of the starting materials with concomitant appearance of a new dihafnocene product, **15**, along with some unidentified decomposition products. Analysis of the product mixture by ^{1}H NMR spectroscopy established that the epoxide had undergone an E_2 elimination, as evidenced by the appearance of vinyl protons at 6.03 and 7.55 ppm with typical trans coupling ($^3J_{HH}$ = 12.3 Hz). The now ubiquitous μ-imido N−H resonance was located as a singlet at 6.18 ppm,which split into a doublet ($^1J_{NH}$ = 47.4 Hz) upon ^{15}N labeling. The ^{15}N NMR spectrum of **15** is presented in Figure 9, and a possible mechanism for the formation of **15** is presented in Scheme 4. The desired product **15** was isolated more cleanly by performing the reaction with the base-stabilized nitrido complex and heating the solution to 65 °C for 2 h. Bergman and co-workers observed elimination reactions with epoxides bearing hydrogens β to the heterocyclic ring and proposed a concerted deprotonation mechanism to account for their formation. However with styrene oxide, cycloaddition was observed upon addition to zirconocene imido complexes.[34b]

■ CONCLUDING REMARKS

The reactivity of a base-free hafnium nitride prepared via CO-induced N_2 cleavage toward dihydrogen and a variety of activated π systems has been investigated. Facile 1,2-addition of dihydrogen across the hafnium−nitrogen linkage prompted the investigation of the chemistry of alkynes and allenes with a view toward developing N−C bond forming reactions directly from dinitrogen. N−H bond formation via C−H addition was observed upon addition of terminal alkynes and bulky allenes, while the desired cycloaddition reactivity was achieved by using sterically unencumbered monosubstituted allenes. Attempts to

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extend this N−C bond forming chemistry to carbonyl- and imine-containing substrates resulted in exclusively N−H bond forming chemistry, often accompanied by the formation of enolate species; this chemistry highlights the tremendous latent basicity of the dihafnium nitride. Finally, efforts to mimic group 4 imido N−C bond forming chemistry with the N_2-derived nitrido ligand upon treatment with epoxides were unsuccessful, providing only elimination products. These results, coupled with our previous work on the reaction chemistry of the base-free dihafnium nitride,[16,17] have established organometallic routes to a large number of small organic molecules directly from CO, N_2, and appropriately selected substrates.

EXPERIMENTAL SECTION[35]

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.[36] Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Other reagents were typically dried over calcium hydride for 24 h before being vacuum-distilled and used immediately. The hafnocene nitride compounds $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(4\text{-}OMe\text{-}pyridine)(\mu_2\text{-}N)$ (**2**) and $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(\mu_2\text{-}N)$ (**1**) were prepared according to literature procedures.[15,16] Allenes were prepared according to literature procedures and dried over CaH_2 before use.[37]

^{1}H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. ^{13}C NMR spectra were recorded on a Bruker 500 spectrometer operating at 125.71 MHz. ^{13}C chemical shifts are reported relative to $SiMe_4$ using chemical shifts of the solvent as a secondary standard where applicable. ^{15}N NMR spectra were recorded on a Bruker 500 spectrometer operating at 50.663 MHz, and ^{15}N chemical shifts are reported relative to liquid NH_3 using an external standard. All coupling constants are reported in hertz. Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

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 molybdenum and copper X-ray tubes (λ = 0.71073 and 1.54184 Å, respectively). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. 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.

Preparation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2\text{-}NH)(\mu_2\text{-}NC(H)O)$ (3). A J. Young NMR tube was charged with 0.012 g (0.015 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\eta^2\text{:}\eta^2\text{-}N_2)$ and 0.450 g of benzene. The solution was frozen while the tube was attached to the high-vacuum line and degassed, and approximately 1 equiv of CO was added at 77 K via calibrated gas volume. The tube was thawed and shaken vigorously for 10 s; the contents turned dark red, signaling formation of **1**. The tube was reattached to the high-vacuum line, and 1 atm of H_2 gas was added at 77 K. The solution was thawed and shaken and allowed to stand at 23 °C for 1 h, whereupon the volatiles were removed in vacuo and the resultant residue was washed with pentane to afford 0.028 g (0.032 mmol, 70% yield from three combined tubes) of an analytically pure white solid. Colorless crystals suitable for X-ray diffraction were obtained by cooling a concentrated fluorobenzene/pentane solution to −35 °C for 2 days. Anal. Calcd for $C_{33}H_{46}Hf_2N_2O$: C, 46.98; H, 5.50; N, 3.32. Found: C, 46.55; H, 5.28; N, 2.98. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.99 (s, 6H, C_5H_2-1,2,4-Me_3), 2.07 (br s overlapped, 18H, C_5H_2-1,2,4-Me_3), 2.09 (br s, 6H, C_5H_2-1,2,4-Me_3), 2.14 (br s, 6H, C_5H_2-1,2,4-Me_3), 4.11 (br d, $^1J_{NH}$ = 61.8, 1H, N*H*), 5.55 (br m overlapped, 4H, C_5H_2-1,2,4-Me_3), 5.69 (br m overlapped, 4H, C_5H_2-1,2,4-Me_3), 9.60 (dd, $^1J_{CH}$ = 187.6, $^2J_{NH}$ = 9.4, 1H, NC(*H*)O). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 13.1, 13.7, 14.7, 14.9, 15.6 (C_5H_2-1,2,4-Me_3), 107.9, 109.4, 110.8, 112.0, 113.1, 113.3, 115.8, 116.8, 117.8 (C_5H_2-1,2,4-Me_3), 171.2 (br s, NC(H)O); two cyclopentadienyl resonances not located (resonances significantly broadened). ^{15}N NMR (benzene-d_6, 23 °C): δ 248.5 (br d, $^1J_{NH}$ = 61.8, *N*H), one nitrogen resonance not located. IR (benzene-d_6): ν_{CN} 1576, 1268 cm^{-1}, $\nu^{13}C^{15}N$ 1562, 1255 cm^{-1}.

Preparation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(CCPh)(\mu_2\text{-}NH)$ (4). A thick-walled glass vessel was charged with 0.065 g (0.080 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2\text{:}\eta^2\text{-}N_2)$ and 1.5 mL of benzene. The vessel containing the dark purple solution was transferred onto a high-vacuum line and degassed, and 1 equiv of CO gas was added at 77 K. An immediate color change to dark red was observed. The resulting solution was degassed and transferred into the glovebox, and 8.6 μL (0.080 mmol) of phenylacetylene was added via microsyringe. The solution was stirred for 1 h at room temperature. The volatiles were removed from the solution in vacuo, and the resulting brown residue was dissolved in a 10/1 diethyl ether/pentane mixture and stored at −35 °C to afford 0.053 g (0.056 mmol, 70% yield) of an analytically pure yellow-brown solid identified as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(CCPh)(\mu_2\text{-}NH)$. Anal. Calcd for $C_{41}H_{50}Hf_2N_2O$: C, 52.17; H, 5.34; N, 2.97. Found: C, 52.53; H, 4.98; N, 2.81. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.78 (s, 6H, C_5H_2-1,2,4-Me_3), 1.95 (s, 6H, C_5H_2-1,2,4-Me_3), 2.12 (s, 6H, C_5H_2-1,2,4-Me_3), 2.21 (s, 6H, C_5H_2-1,2,4-Me_3), 2.24 (s, 6H, C_5H_2-1,2,4-Me_3), 2.50 (s, 6H, C_5H_2-1,2,4-Me_3), 5.05 (d, 2H, $^4J_{HH}$ = 2.5, C_5H_2-1,2,4-Me_3), 5.15 (d, 2H, $^4J_{HH}$ = 2.5, C_5H_2-1,2,4-Me_3), 5.82 (d, 2H, $^4J_{HH}$ = 2.5, C_5H_2-1,2,4-Me_3), 6.04 (d, 2H, $^4J_{HH}$ = 2.5, C_5H_2-1,2,4-Me_3), 6.99 (d, 1H, $^3J_{HH}$ = 7.2, Ar C*H*), 7.01 (br s. overlapped, 1H, μ-N*H*), 7.09 (t, 2H, $^3J_{HH}$ = 7.2, Ar C*H*), 7.60 (d, 2H, $^3J_{HH}$ = 7.0, Ar C*H*). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 13.1, 13.9, 14.0, 15.2, 15.3, 15.4 (C_5H_2-1,2,4-Me_3), 110.7, 111.7, 115.1, 116.0, 116.3, 117.4, 117.9, 118.5, 121.0, 123.5, (C_5H_2-1,2,4-Me_3), 125.1, 127.0, 127.8, 129.0, 131.4, 132.7 (Ar-*C* or alkene C), 135.7 (d, $^1J_{CN}$ = 32.6, NCO). ^{15}N NMR (benzene-d_6, 23 °C): δ 91.7 (d, $^1J_{CN}$ = 32.6, *N*CO), 282.1 (d, $^1J_{NH}$ = 45.4, μ-*N*H). IR (benzene-d_6): ν_{NH} 3575 cm^{-1}, ν_{NCO} 2221 cm^{-1}, $\nu^{15}N^{13}CO$ 2135 cm^{-1}, ν_{CC} 2085 cm^{-1}.

Preparation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(NCO)(Me,SiMe_3\text{-}C{=}C{=}CH)(\mu_2\text{-}NH)$ (6). A J. Young NMR tube was charged with 0.012 g (0.015 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\eta^2\text{:}\eta^2\text{-}N_2)$ and 0.450 g of benzene. The solution was frozen at the high-vacuum line and degassed, and 1 equiv of CO was added at 77 K. The tube was thawed and shaken vigorously for 10 s; the contents turned dark red, signaling the formation of **1**. The tube was quickly degassed and transferred into the glovebox, where 3.0 μL (0.030 mmol) of 1-methyl-1-trimethylsilylallene was added via microsyringe. The reaction mixture was left at room temperature for 1 h before the volatiles were removed in vacuo and the oily red residue was washed with cold pentane (2 × 5 mL) to yield 0.039 g (0.040 mmol, 66% yield from four combined tubes) of an analytically pure off-white powder. Colorless crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a concentrated fluorobenzene solution over 4 days at −35 °C. Anal. Calcd for $C_{40}H_{58}Hf_2N_2OSi$: C, 49.63; H, 6.04; N, 2.89. Found: C, 49.31; H, 5.71; N, 2.80. ^{1}H NMR (benzene- d_6, 23 °C): δ 0.35 (s, 9H, allene SiMe_3), 1.73 (s, 3H, C_5H_2-1,2,4-Me_3), 1.77 (s, 3H, C_5H_2-1,2,4-Me_3), 1.94 (s, 3H, C_5H_2-1,2,4-Me_3), 1.97 (s, 3H, C_5H_2-1,2,4-Me_3), 1.98 (s, 3H, allene *Me*), 2.06 (s, 3H, C_5H_2-1,2,4-Me_3), 2.07 (s, 3H, C_5H_2-1,2,4-Me_3), 2.08 (s, 3H, C_5H_2-1,2,4-Me_3), 2.09 (s, 3H, C_5H_2-1,2,4-Me_3), 2.14 (s, 3H, C_5H_2-1,2,4-Me_3), 2.15 (s, 3H, C_5H_2-1,2,4-Me_3), 2.20 (s, 3H, C_5H_2-1,2,4-Me_3), 5.07 (q, $^3J_{HH}$ = 3.7, 1H, allene C*H*), 5.11 (d, $^4J_{HH}$ = 2.4, 1H, C_5H_2-1,2,4-Me_3), 5.12 (d, $^4J_{HH}$ = 2.4, 1H, C_5H_2-1,2,4-Me_3), 5.40 (d, $^4J_{HH}$ = 2.4, 1H, C_5H_2-1,2,4-Me_3), 5.66

dx.doi.org/10.1021/om500393n | *Organometallics* 2014, 33, 3727−3737

(d, $^4J_{HH}$ = 2.4, 1H, C_5H_2-1,2,4-Me_3), 5.66 (d, $^4J_{HH}$ = 2.4, 1H, C_5H_2-1,2,4-Me_3), 5.82 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 6.43 (d, $^1J_{NH}$ = 45.6, 1H, N*H*). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ −0.1 (allene SiMe_3), 13.0, 13.0, 13.7, 13.8, 13.8, 13.9, 14.0, 14.0, 15.2, 15.3, 15.4, 15.5 (C_5H_2-1,2,4-Me_3), 16.7 (allene *Me*), 69.8 (allene CH), 110.3 (*C*(Me)SiMe_3), 111.9, 111.9, 113.8, 113.9, 114.4, 114.6, 115.4, 115.9, 116.0, 117.0, 117.5, 117.6, 118.2, 118.2, 118.4, 118.4, 119.6, 121.3, 125.0, 126.5 (C_5H_2-1,2,4-Me_3), 135.7 (d, $^1J_{CN}$ = 33.3, NCO), 208.3 (allene *C*). ^{15}N NMR (benzene-d_6, 23 °C) δ 91.5 (d, $^1J_{CN}$ = 33.3, *N*CO), 279.9 (d, $^1J_{NH}$ = 45.6, *N*H). IR (benzene-d_6): ν_{NH} 3473 cm^{-1}, ν_{NCO} 2162 cm^{-1}, ν_{NCO} 2135 cm^{-1}, ν_{CC} 1881 cm^{-1}.

Preparation of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2,κ^2*N*-MeOHC=C=CH_2) (9-OMe). 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-N_2) and 0.450 g of benzene. The contents of the tube were frozen at the high-vacuum line and degassed, and approximately 1 equiv of CO was added at 77 K. The tube was thawed and shaken vigorously for 10 s; the contents turned dark red, signaling the formation of **1**. The tube was quickly degassed and transferred into the glovebox, whereupon 1.4 μL (0.016 mmol) of methoxyallene was added via microsyringe. The reaction mixture was allowed to stand at room temperature for 2 h before the volatiles were removed in vacuo and the oily red residue was washed with cold pentane (2 × 5 mL) to yield 0.056 g (0.063 mmol, 66% from six combined tubes) of an analytically pure white powder. Colorless crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated fluorobenzene solution stored at −35 °C for 18 h. The reaction has proven difficult to scale due to the sensitivity to the amount of added carbon monoxide. As such, it has proven more convenient to repeat the reaction on the reported scale rather than attempting to scale the reaction. Anal. Calcd for $C_{37}H_{50}Hf_2N_2O_2$: C, 48.74; H, 5.53; N, 3.07. Found: C, 48.39; H, 5.32; N, 2.88. ^1H NMR (benzene- d_6, 23 °C): δ 1.77 (s, 6H, C_5H_2-1,2,4-Me_3), 1.78 (s, 6H, C_5H_2-1,2,4-Me_3), 2.03 (s, 6H, C_5H_2-1,2,4-Me_3), 2.07 (s, 6H, C_5H_2-1,2,4-Me_3), 2.23 (s, 6H, C_5H_2-1,2,4-Me_3), 2.45 (s, 6H, C_5H_2-1,2,4-Me_3), 3.36 (d, $^4J_{HH}$ = 2.8, 2H, allene CH_2), 3.43 (s, 3H, O*Me*), 5.14 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.34 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.77 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.78 (t, $^4J_{HH}$ = 2.8, 1H, allene *CH*), 5.94 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 12.6, 13.0, 13.4, 13.8, 14.7, 15.0 (C_5H_2-1,2,4-Me_3), 39.3 (N-CH_2), 58.2 (O*Me*), 112.5, 112.7, 113.2, 113.3, 113.3, 113.4, 117.4, 118.0, 121.3, 121.9 (C_5H_2-1,2,4-Me_3), 134.5 (d, $^1J_{CN}$ = 32.7, NCO), 142.2 (allene *CH*), 168.0 (allene *C*). ^{15}N NMR (benzene-d_6, 23 °C) δ 86.8 (d, $^1J_{CN}$ = 31.9, *N*CO), 269.0 (s, Hf-*N*-Hf). IR (benzene-d_6): ν_{NCO} 2078 cm^{-1}, $\nu^{15}N^{13}CO$ 2009 cm^{-1}, ν_{CC} 1999 cm^{-1}.

Preparation of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-NH)-(OCH_2=CCMe_3) (10). A thick-walled glass vessel was charged with 0.060 g (0.072 mmol) of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(μ_2,η^2:η^2-N_2) and dissolved in 2.0 mL of benzene. The vessel containing the dark purple solution was transferred to a high-vacuum line and degassed, and CO gas (1 equiv at 77 K) was added via calibrated gas volume. An immediate color change to dark red was observed, signaling the formation of **1**. The resulting solution was degassed, brought into the glovebox, and transferred to a 20 mL scintillation vial, and 10.2 μL (0.080 mmol) of pinacolone was added via microsyringe. The solution was stirred for 1 h at 23 °C before the volatiles were removed in vacuo. Recrystallization from THF/pentane yielded 0.040 g (0.043 mmol, 60% yield) of colorless diamonds identified as [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-NH)(OCH_2=CCMe_3). Anal. Calcd for $C_{39}H_{56}Hf_2N_2O_2$: C, 49.73; H, 5.99; N, 2.97. Found: C, 49.69; H, 5.79; N, 2.71.^1H NMR (benzene-d_6, 23 °C): δ 1.27 (s, 9H, C(O)CMe_3), 1.81 (s, 6H, C_5H_2-1,2,4-Me_3), 2.06 (s, 6H, C_5H_2-1,2,4-Me_3), 2.08 (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), 2.26 (s, 6H, C_5H_2-1,2,4-Me_3), 3.66 (s, 1H, acyl CH_2), 4.24 (s, 1H, acyl CH_2), 5.23 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3), 5.75 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3), 5.89 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3), 6.08 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3), 6.56 (d, $^1J_{NH}$ = 45.8, 1H, N*H*). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 12.9, 13.1, 13.7, 13.9, 14.8, 15.4 (C_5H_2-1,2,4-Me_3), 29.3 (CMe_3), 38.1 (CMe_3), 86.8 (acyl CH_2), 112.5, 112.7, 113.6, 116.5, 116.7, 117.2, 117.4, 118.2, 122.6, 126.1 (C_5H_2-1,2,4-Me_3), 135.8 (d, $^1J_{NC}$ = 32.4, NCO), 175.5 (ketone C(O)). ^{15}N NMR (benzene-d_6, 23 °C): δ 88.7 (d, $^1J_{NC}$ = 32.4, *N*CO), 258.2 (d, $^1J_{NH}$ = 45.8, *N*H). IR (benzene): ν_{NH} 3472 cm^{-1}, ν_{NCO} 2211 cm^{-1}, $\nu^{15}N^{13}CO$ 2143 cm^{-1}, ν_{CC} 1707 cm^{-1}.

Preparation of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-NH)(NH_2) (14). A thick-walled glass vessel was charged with 0.060 g (0.075 mmol) of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(μ_2,η^2:η^2-N_2), and this complex was dissolved in 1.5 mL of benzene. The vessel containing the solution was transferred to the high-vacuum line and degassed, and 1 equiv of CO was added at 77 K via a calibrated gas volume. Thawing the solution resulted in an immediate color change to dark red, whereupon the contents of the vessel were refrozen and ammonia (72 Torr from 31.6 mL bulb, 0.125 mmol) was added via calibrated gas volume. The reaction mixture was allowed to stand at 23 °C for 1 h before the solvent was removed in vacuo and the residue redissolved in a 10/1 fluorobenzene/pentane mixture. Storage at −35 °C resulted in deposition of 0.051 g (0.060 mmol, 80% yield) of colorless blocks suitable for X-ray diffraction identified as [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-NH)(NH_2). Anal. Calcd for $C_{33}H_{47}Hf_2N_3O$: C, 46.16; H, 5.52; N, 4.89. Found: C, 45.80; H, 5.03; N, 4.48. ^1H NMR (benzene-d_6, 23 °C): δ 1.74 (s, 6H, C_5H_2-1,2,4-Me_3), 1.84 (s, 6H, C_5H_2-1,2,4-Me_3), 1.97 (s, 6H, C_5H_2-1,2,4-Me_3), 2.12 (s, 6H, C_5H_2-1,2,4-Me_3), 2.12 (s, 6H, C_5H_2-1,2,4-Me_3), 2.22 (s, 6H, C_5H_2-1,2,4-Me_3), 3.12 (br s, 2H, NH_2), 5.11 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3), 5.19 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3), 5.39 (d, $^1J_{NH}$ = 45.8, *N*H), 5.65 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3), 5.98 (d, $^4J_{HH}$ = 2.5, 2H, C_5H_2-1,2,4-Me_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 13.1, 13.3, 13.4, 13.9, 15.4, 15.5 (C_5H_2-1,2,4-Me_3), 109.8, 111.2, 113.5, 113.6, 116.6, 116.6, 117.1, 117.6, 120.3, 124.0 (C_5H_2-1,2,4-Me_3), 135.1 (d, $^1J_{CN}$ = 32.8, NCO). ^{15}N NMR (benzene-d_6, 23 °C): δ 83.7 (d, $^1J_{CN}$ = 32.8, *N*CO), 261.4 (d, $^1J_{NH}$ = 45.8, *N*H). IR(benzene-d_6): ν_{NH} 3568 cm^{-1}, ν_{NH_2} 3430 cm^{-1}, ν_{NCO} 2209 cm^{-1}, $\nu^{15}N^{13}CO$ 2143 cm^{-1}.

Preparation of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-NH)(OCH=CHPh) (15). A thick-walled glass vessel was charged with 0.075 g (0.092 mmol) of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(μ_2,η^2:η^2-N_2) and 2 mL of benzene. Via microsyringe, 9.4 μL (0.094 mmol) of 4-methoxypyridine was added, and a color change to deep green was observed. The vessel was removed from the glovebox, its contents were frozen, and 1 atm of CO gas was admitted at 77 K. The resulting reaction mixture was warmed to room temperature and shaken vigorously to produce a dark red solution, signaling the formation of **2**. The vessel was degassed and brought into the glovebox, and 11.6 μL (0.102 mmol) of styrene oxide was added via microsyringe. The solution was heated to 65 °C for 2 h before the volatiles were removed in vacuo and the oily yellow residue was washed with 20 mL of cold pentane to afford 0.080 g (0.083 mmol, 90% yield) of a yellow solid identified as [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-NH)(OCH=CHPh). Anal. Calcd for $C_{41}H_{52}Hf_2N_2O_2$: C, 51.20; H, 5.45; N, 2.91. Found: C, 50.94; H, 5.11; N, 2.51. ^1H NMR (benzene-d_6, 23 °C): δ 1.82 (s, 6H, C_5H_2-1,2,4-Me_3), 1.92 (s, 6H, C_5H_2-1,2,4-Me_3), 2.08 (s, 6H, C_5H_2-1,2,4-Me_3), 2.09 (s, 6H, C_5H_2-1,2,4-Me_3), 2.11 (s, 6H, C_5H_2-1,2,4-Me_3), 2.23 (s, 6H, C_5H_2-1,2,4-Me_3), 5.19 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.49 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 5.81 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 6.00 (d, $^4J_{HH}$ = 2.4, 2H, C_5H_2-1,2,4-Me_3), 6.03 (d, 1H, $^3J_{HH}$ = 12.3, vinyl *CH*), 6.18 (d, $^1J_{NH}$ = 47.4, 1H, N*H*), 7.00 (m, 1H, aryl *CH*), 7.18 (t, $^3J_{HH}$ = 7.3, 2H, aryl *CH*), 7.32 (d, $^3J_{HH}$ = 7.2, 2H, aryl *CH*), 7.75 (d, 1H, $^3J_{HH}$ = 12.3, vinyl *CH*). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 13.1, 13.4, 14.0, 14.0, 15.3, 15.5 (C_5H_2-1,2,4-Me_3), 110.3 (alkene *CH*), 111.7, 113.5, 114.8, 116.0, 116.3, 116.9, 117.5, 117.8, 124.6, 124.9 (C_5H_2-1,2,4-Me_3), 125.3 (aryl CH), 125.4 (aryl CH), 129.3 (aryl CH), 135.4 (d, $^1J_{CN}$ = 33.0, NCO), 139.0 (ipso *C*), 152.3 (O-vinyl CH). ^{15}N NMR (benzene-d_6, 23 °C) δ 86.7 (d, $^1J_{CN}$ = 33.0, *N*CO), 259.4 (d, $^1J_{NH}$ = 47.4, *N*H). IR (KBr): ν_{NH} 3569 cm^{-1}, ν_{NCO} 2221 cm^{-1}, $\nu^{15}N^{13}CO$ 2133 cm^{-1}, ν_{CC} 1621 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and CIF files giving additional experimental procedures, crystallographic details for **3**, **6**−**8**, **9-OMe**, **9-Tol**,

dx.doi.org/10.1021/om500393n | *Organometallics* 2014, 33, 3727−3737

10, **11**, and **14**, and representative NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for P.J.C.: pchirik@princeton.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Director of the Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy (DE-SC0006498), for financial support.

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(35) Representative experimental procedures are presented here. Complete preparations as well as spectroscopic data and additional NMR figures are presented in the Supporting Information.

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