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Carbon Monoxide-Induced Dinitrogen Cleavage with Group 4 Metallocenes: Reaction Scope and Coupling to N−H Bond Formation and CO Deoxygenation

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Abstract: The scope of CO-induced N_2 cleavage in a series of zirconocene and hafnocene complexes containing activated, side-on bound dinitrogen ligands has been studied. In each case, bridging oxamidide ligands, $[N_2C_2O_2]^{4-}$, were formed from N−N bond cleavage coupled to N−C and C−C bond assembly. For the zirconium examples, $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, dinitrogen loss became competitive with N_2 carbonylation, and significant quantities of the zirconocene dicarbonyl accompanied oxamidide formation. In contrast, the hafnocene complex $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ underwent clean carbonylative dinitrogen cleavage with no evidence of N_2 loss. CO-induced N_2 cleavage was also coupled to N−H bond formation by hydrogenation and C−H bond activation, as carbonylation of the zirconocene and hafnocene dinitrogen complexes in the presence of H_2 or phenylacetylene furnished isocyanato metallocene complexes with bridging imido (μ-NH) ligands. In the case of the *ansa*-hafnocene dinitrogen complex, replacing the dihydrogen atmosphere with various primary silanes yielded an isocyanato hafnocene μ-oxo hydride resulting from cleavage of N_2 and CO, the diatomics with the two strongest bonds in chemistry.

Introduction

Synthetic transformations that couple the cleavage of the strong nonpolar bond of molecular nitrogen, N_2, with nitrogen−carbon bond formation are desirable, given the utility of nitrogen-containing organic molecules as fertilizers, pharmaceuticals, dyes, semiconductors, and fibers.[1,2] Dinitrogen is an attractive feedstock because of its atmospheric abundance, accessibility, and nontoxicity. However, the strong N≡N triple bond (225 kcal/mol) and the absence of a dipole moment present significant kinetic and thermodynamic obstacles for reactivity.[3] Currently, N_2 enters the biological nitrogen cycle by fixation to ammonia through proton-coupled electron transfer with nitrogenase enzymes[4] or industrially by hydrogenation to NH_3 using the well-established high-temperature and -pressure conditions of the Haber−Bosch process.[1,5−7] The direct conversion of N_2 to nitrogen-containing organic molecules offers the potential for substantial energy and fossil fuel savings.[8]

Like N_2, carbon monoxide is a diatomic molecule with a very strong triple bond (257 kcal/mol). Selective formation of carbon−carbon bonds from CO as a component of syngas is a long-standing challenge in catalysis as an alternative to the nonselective Fischer−Tropsch process.[9,10] Direct homologation of CO is also attractive, although it is challenging and has little precedent. Early examples include formation of ethylenediolate dianion, $[C_2O_2]^{2-}$, and higher cyclic molecules from exposure of CO to molten alkali metals such as Na/K alloy.[11,12] With soluble organometallic compounds, pioneering studies by Evans and co-workers described the formation of a ketenecarboxylate bridging ligand, $[O_2CCCO]^{2-}$, upon addition of 90 psi CO to the THF derivative of decamethylsamarocene, $(\eta^5\text{-}C_5Me_5)_2\text{-}Sm(THF)_2$.[13] More recently, Cloke and co-workers reported selective trimerization of CO to the deltate dianion, *cyclo*-$[C_3O_3]^{2-}$, from carbonylation of the U(III) complex (η^5-

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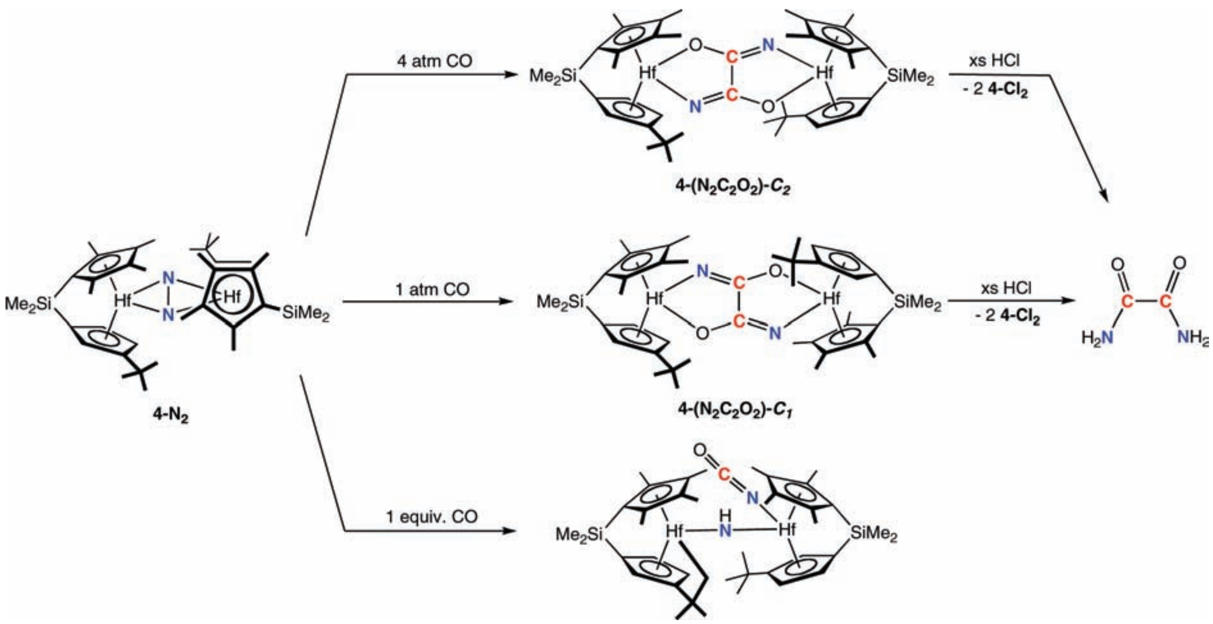
Scheme 1. CO-Induced N_2 Cleavage Promoted by an *ansa*-Hafnocene Complex



$C_5Me_5)(\eta^8$-1,4-$(Si^iPr_3)_2$-$C_8H_6)U(THF)$.[14] Replacing the (η^5-C_5Me_5) ligand in the uranium compound with the less-substituted (η^5-C_5Me_4H) ring resulted in selective tetramerization to the squarate dianion, $[C_4O_4]^{2-}$.[15] The mechanism of the C−C bond-forming process was explored with isotopic labeling studies and density functional theory calculations, and it was concluded that the uranium acts as both a reductant for the C≡O bond and an electrophile for formation of isocarbonyl intermediates that orient the CO ligands for the C−C bond-forming event.[16]

Because N_2 and CO are isoelectronic, we sought to develop new reactions that couple these two diatomics in an “aza-variant” of CO homologation. Evans and co-workers reported N−N bond cleavage in azobenzene upon carbonylation of a decamethylsamarocene complex.[17,18] Group 4 transition-metal dinitrogen compounds, particularly those with side-on (μ_2,η^2,η^2) coordination,[19,20] seemed well-suited for this purpose because of the rich N_2 functionalization chemistry known for this structural type. Various N−H bond-forming reactions, including N_2 hydrogenation,[21−24] addition of hydrocarbon C−H bonds,[23,25] protonolysis with weak Brønsted acids,[24,26,27] and silylation followed by hydrolysis, have all been reported.[28] Considerable attention is now being devoted to N−C bond-forming reactions, and examples of alkyne[29] and isocyanate[30] cycloaddition and CO_2 insertion[31,32] have been observed and augment known N_2 functionalization reactions derived from treatment of coordinated dinitrogen with various carbon-based electrophiles.[33−36]

Our laboratory recently reported the synthesis of the *ansa*-hafnocene $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**4-N₂**) by sodium amalgam reduction of the corresponding hafnocene diiodide.[37] The N−N bond length of 1.457(5) Å determined by X-ray diffraction is the longest of any group 4 metallocene dinitrogen complex, although it is shorter than the values reported for the nonmetallocene zirconium and hafnium N_2 compounds prepared by Fryzuk[19,38,39] and Sita.[35] Addition of 1−4 atm CO to **4-N₂** resulted in N−N bond cleavage with assembly of one C−C and two N−C bonds (Scheme 1). At higher CO pressures, the C_2-symmetric hafnocene oxamidide complex **4-(N₂C₂O₂)-*C₂*** was observed, while with 1 atm CO, the C_1-symmetric isomer, **4-(N₂C₂O₂)-*C₁***, predominated. Treatment of either *ansa*-hafnocene oxamidide complex with a Brønsted acid furnished oxamide, $H_2NC(O)C(O)NH_2$, demonstrating that an important agrochemical can be synthesized, albeit stoichiometrically, from N_2 and CO, the diatomics with the two strongest bonds in chemistry.

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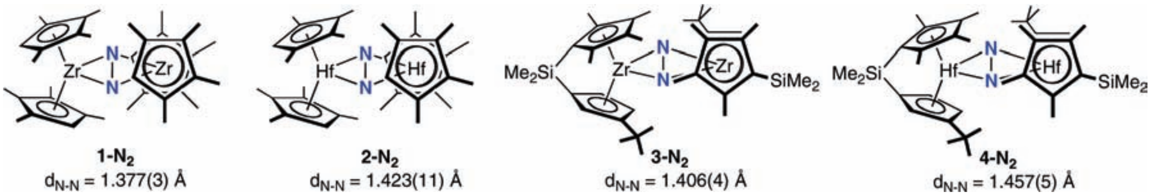
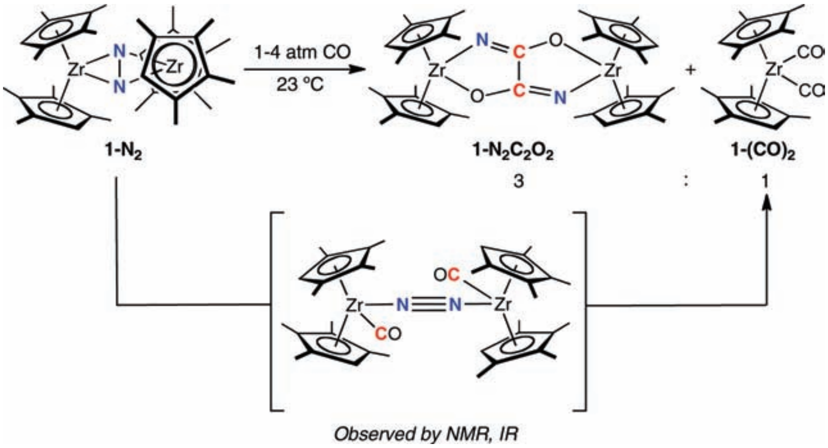


Figure 1. Zirconocene and hafnocene dinitrogen complexes with side-on bound N_2 ligands, the corresponding N−N bond distances, and the compound numbering scheme used in this study.

Scheme 2. Carbonylation of **1-N$_2$**



Ligand-induced N_2 bond cleavage has been reported previously by Fryzuk and co-workers with a phosphino(diamide)-ligated tantalum complex containing a side-on, end-on bound dinitrogen ligand.[40] Addition of various hydride reagents such as boranes, alanes, silanes, and a zirconium hydride resulted in cleavage of the N−N bond and yielded functionalized imides and nitrides. In group 4 metallocene chemistry, the facile carbonylation of **4-N$_2$** has raised questions regarding the scope of CO-induced bond cleavage and the generality of the transformation, particularly with compounds that contain more weakly activated side-on bound N_2 ligands. The lengthy synthesis of **4-N$_2$** and low natural abundance of hafnium have also inspired exploration of N_2 carbonylation with more abundant metals such as titanium and zirconium. For the former, Sobota reported that addition of CO to "$TiNMg_2Cl_2(THF)$" (prepared from reduction of $TiCl_4(THF)_2$ with Mg under a N_2 atmosphere) followed by addition of CH_3I furnished *N*,*N*-dimethylformamide (DMF), demonstrating that lighter group 4 congeners promote the desired CO-induced N_2 bond cleavage chemistry.[41] In group 5 chemistry, carbonylation of terminal vanadium nitrides has also been reported, although the nitrogen atoms were not derived directly from N_2 cleavage.[42,43] Here we describe a more systematic study of CO-induced N_2 bond cleavage and expand the scope of this reaction by using carbon monoxide as a trigger for dinitrogen scission coupled to N−H bond formation by hydrogenation.

Results and Discussion

Scope of CO-Induced Dinitrogen Cleavage. The discovery of CO-induced N−N bond cleavage with the *ansa*-hafnocene dinitrogen complex **4-N$_2$** prompted an exploration of the scope of this transformation with other group 4 metallocene complexes with less activated, side-on bound N_2 ligands. The compounds used in this study along with the crystallographically determined N−N bond distances and compound numbering scheme are presented in Figure 1.

Each of the dinitrogen compounds presented in Figure 1 was studied for N_2 carbonylation. Addition of 4 atm CO to the compound with the least activated dinitrogen ligand in the series, $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**1-N$_2$**), furnished two products in a 3:1 ratio (Scheme 2). The major product was identified as the zirconocene oxamidide compound $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(N_2C_2O_2)$ (**1-N$_2$C$_2$O$_2$**) arising from CO-induced dinitrogen cleavage. As shown in Table 1, **1-N$_2$C$_2$O$_2$** exhibits ^{1}H, ^{13}C, and ^{15}N NMR spectral features diagnostic of an oxamidide ligand.[37] Particularly noteworthy is the observation of $^1J_{C-N} = 3.7$ Hz upon preparation of **1-^{15}N$_2$^{13}C$_2$O$_2$** using $^{15}N_2$ and ^{13}CO gases. The ^{13}C isotopologue **1-N$_2$^{13}C$_2$O$_2$** was also synthesized and exhibited the same ^{13}C NMR shift but lacked the $^{13}C-^{15}N$ coupling.

The minor product of carbonylation of **1-N$_2$** was identified as $(\eta^5\text{-}C_5Me_4H)_2Zr(CO)_2$ (**1-(CO)$_2$**),[44] indicating that dinitrogen loss competes with ligand-induced N_2 bond cleavage (Scheme 2). Reducing the CO pressure to 1 atm also formed **1-N$_2$C$_2$O$_2$**

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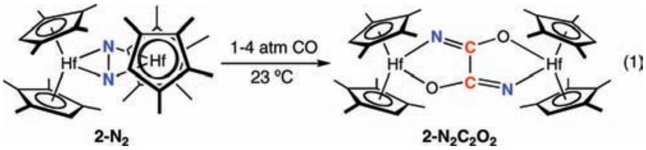
Table 1. NMR Spectroscopic Data for the Zirconocene and Hafnocene Oxamidide Complexes Prepared from CO-Induced N_2 Bond Cleavage

compound	δ ^{13}C (ppm)[a]	δ ^{15}N (ppm)[b]	coupling constants[c]
1-$N_2C_2O_2$	162.89	400.4	$^1J_{C-N}$, $^2J_{C-N} = 3.7^d$
2-$N_2C_2O_2$	160.21	376.4	$^1J_{C-N}$, $^2J_{C-N} = 3.9^d$
3-$N_2C_2O_2$-C_1	162.76	392.4	$^1J_{C-N} = 4.0$, $^2J_{C-N} = 4.0$
	164.07	396.5	$^1J_{C-C} = 60.9$
3-$N_2C_2O_2$-C_2	165.39	397.2	$^1J_{C-N}$, $^2J_{C-N} = 3.8^d$
4-$N_2C_2O_2$-C_1[e]	159.93	369.4	$^1J_{C-N} = 5.0$, $^2J_{C-N} = 3.0$
	161.46	370.3	$^1J_{C-C} = 61.4$
4-$N_2C_2O_2$-C_2[e]	162.65	371.3	$^1J_{C-N}$, $^2J_{C-N} = 3.9^d$

[a] Benzene-d_6 ^{13}C NMR shift (ppm) of the $[C_2N_2O_2]^{4-}$ core. [b] Benzene-d_6 ^{15}N NMR shift (ppm) of the $[C_2N_2O_2]^{4-}$ core referenced to NH_3. [c] Values reported in Hz. [d] Values reported as an average for the AA′XX′ spin system. See the Supporting Information for details. [e] Data taken from ref 37.

and **1-$(CO)_2$** in a final 3:1 ratio. Monitoring the reaction by ^{1}H and ^{13}C NMR spectroscopy allowed the observation of $[(\eta^5\text{-}C_5Me_4H)_2Zr(CO)]_2(\mu_2, \eta^1, \eta^1\text{-}N_2)$, which converted to the final product mixture over the course of 1 h at 23 °C. This intermediate is analogous to the permethylzirconocene variant $[(\eta^5\text{-}C_5Me_5)_2Zr(CO)]_2(\mu_2, \eta^1, \eta^1\text{-}N_2)$, which was also prepared by CO addition to the corresponding dinitrogen compound by Bercaw and co-workers more than three decades ago.[45]

More selective carbonylation chemistry was observed with the hafnocene congener $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**2-N_2**). Exposure of a benzene-d_6 solution of **2-N_2** to 1−4 atm CO furnished the hafnocene oxamidide complex **2-$N_2C_2O_2$** (eq 1).



2-N_2 **2-$N_2C_2O_2$** (1)

No evidence for formation of the hafnocene dicarbonyl **2-$(CO)_2$** was observed using NMR and IR spectroscopies. Formation of the oxamidide ligand was definitively established by multinuclear NMR spectroscopy (Table 1) and preparation of ^{13}C and ^{15}N isotopologues (Figure 2). The solid state structure of **2-$N_2C_2O_2$** was determined by single-crystal X-ray diffraction and has the familiar bent metallocene geometry with an essentially planar, bridging oxamidide core (Figure 3). Because of the symmetry of the hafnocene, the oxygen and nitrogen atoms of the $[N_2C_2O_2]^{4-}$ moiety could not be distinguished and are labeled "E" in the depiction presented in Figure 3. The C(37)−C(38) distance of 1.531(8) Å is typical for a carbon−carbon single bond, and the core oxamidide distances of 1.297(7)/1.299(7) Å and 1.303(7)/1.320(8) Å for C(37)−E(2)/E(4) and C(38)−E(1)/E(3) are similar to those found in the related *ansa*-hafnocene oxamidide **4-$N_2C_2O_2$-C_2**.

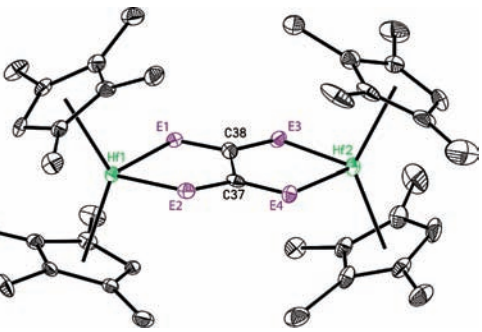


Figure 3. Molecular structure **2-$N_2C_2O_2$** shown using 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. N and O atoms were not distinguished and are labeled "E".

To complete the carbonylation of the series of N_2 compounds presented in Figure 1, 1−4 atm CO was added to the *ansa*-zirconocene dinitrogen compound **3-N_2** (Scheme 3).[46] As was observed for the hafnium congener **4-N_2**, 4 atm CO furnished the C_2-symmetric oxamidide product **3-$N_2C_2O_2$-C_2**, while addition of 1 atm CO yielded exclusively the C_1-symmetric isomer. As with the hafnium congener, we were unable to definitively assign the identity of the C_1-symmetric compound.[37] At both pressures, trace but detectable (<5%) quantities of the dicarbonyl compound **3-$(CO)_2$** were observed.[46] Overall, the CO-induced N_2 carbonylation is a general transformation for both zirconium and hafnium compounds with modestly to strongly activated, side-on bound dinitrogen ligands and is available to compounds that are more readily synthesized than **4-N_2**.

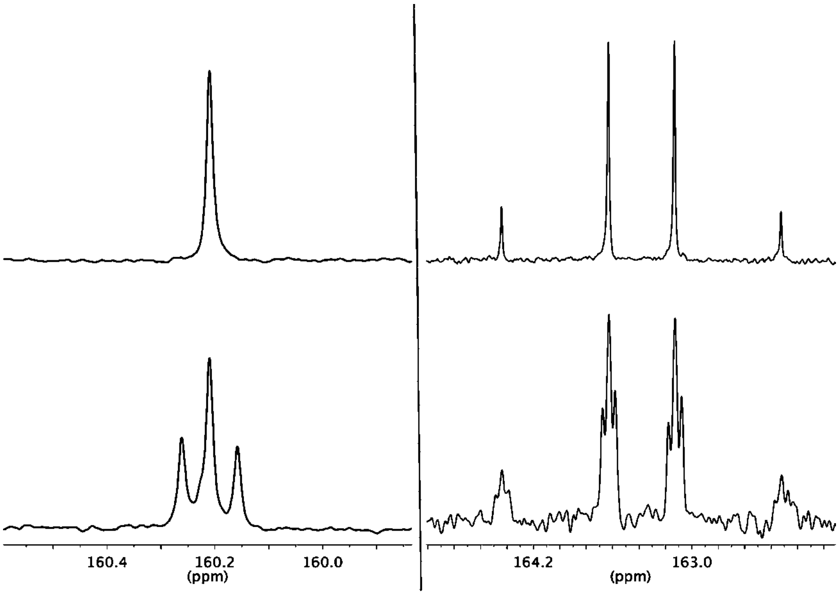


Figure 2. ^{13}C NMR spectra of (top left) **2-$N_2{}^{13}C_2O_2$**, (bottom left) **2-$^{15}N_2{}^{13}C_2O_2$**, (top right) **3-$N_2{}^{13}C_2O_2$-C_1**, and (bottom right) **3-$^{15}N_2{}^{13}C_2O_2$-C_1**.

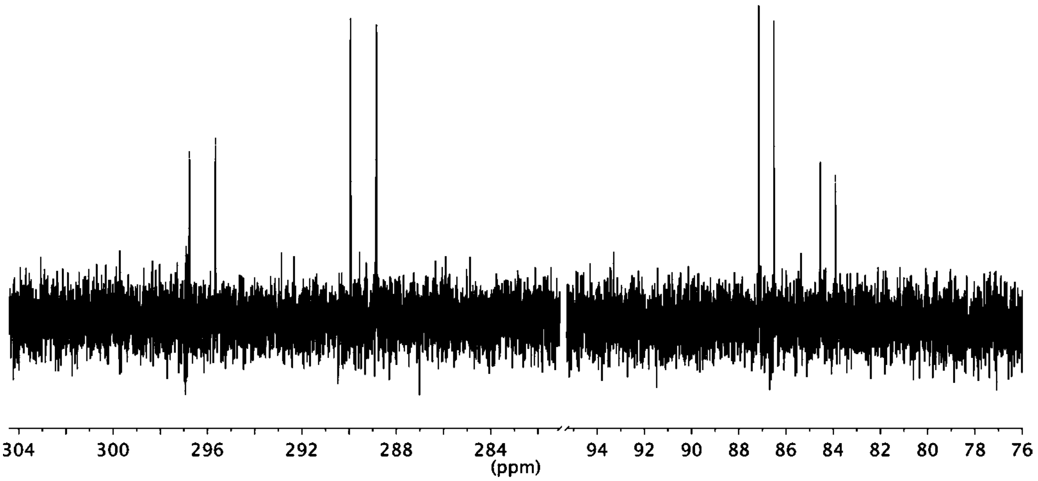
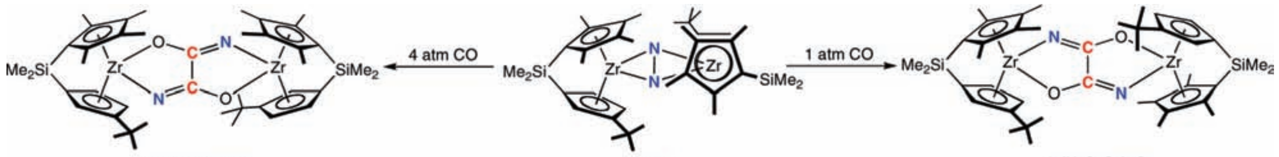


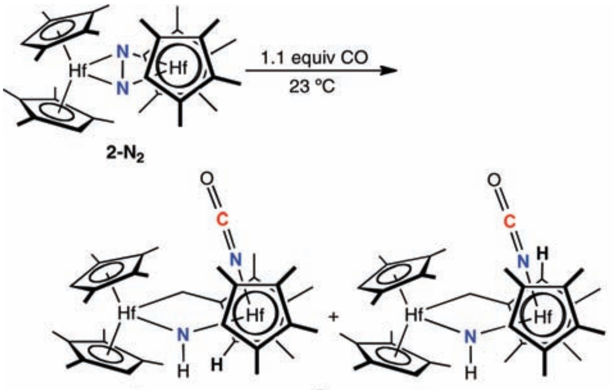
Figure 4. Benzene-d_6 ^{15}N NMR spectrum of the μ-imido region (downfield) and isocyanate region (upfield) of the mixture of isomers of **5-$^{15}N^{13}C$**.

Scheme 3. Carbonylation of **3-N_2** with 1 and 4 atm CO



3-($N_2C_2O_2$)-C_2 **3-N_2** **3-($N_2C_2O_2$)-C_1**

As reported previously for the *ansa*-hafnocene **4-N_2**, slow diffusion of 1.5 equiv of CO gas into a benzene-d_6 solution of the dinitrogen compound resulted in N−N bond cleavage to form a hafnocene product containing a terminal isocyanate and a bridging imido (μ-NH) that arises from cyclometalation of a cyclopentadienyl *tert*-butyl substituent (Scheme 1). Analogous chemistry was explored with the methylated hafnocene dinitrogen complex **2-N_2** to determine whether a similar outcome would be obtained upon removal of the *tert*-butyl group that participates in cyclometalation. Slow diffusion of 1.1 equiv of CO into a benzene-d_6 solution of **2-N_2** over the course of 16 h at 23 °C resulted in a color change from purple to yellow signaling the formation of two new isomeric cyclometalated hafnocene isocyanates, **5**, in an 1.5:1 ratio as judged by multinuclear NMR spectroscopy, IR spectroscopy, and (in one case) X-ray diffraction (eq 2).

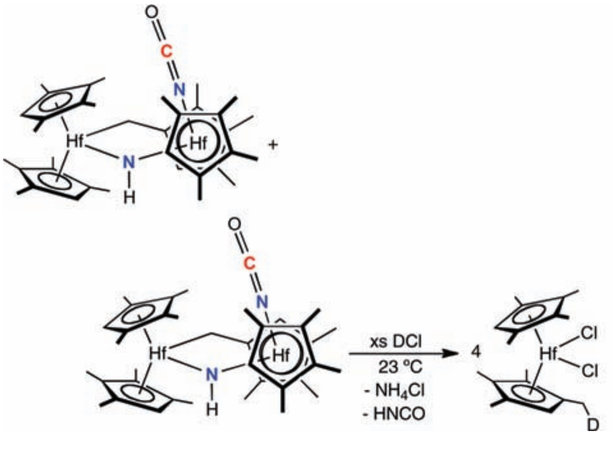


2-N_2 **5** (2)

On a preparative scale, several samples were independently synthesized in NMR tubes and combined and the mixture of isomers isolated. Attempts to separate the isomers by recrystallization at −35 °C produced no change in the ratio of isomers.

Preparation of ^{13}C and ^{15}N isotopologues was accomplished using ^{13}CO and $^{15}N_2$, respectively. Diagnostic regions of the ^{15}N NMR spectrum of **5-$^{15}N^{13}C$** are presented in Figure 4 and confirm the presence of both isocyanate and μ-imido ligands in both isomers. The isocyanate nitrogens appear upfield at 86.8 (major) and 84.2 (minor) ppm in the ^{15}N NMR spectrum and exhibit typical $^1J_{N-C}$ coupling constants of 32.4 and 32.6 Hz. The ^{13}C NMR spectrum of the isotopologues of the same mixture of isomers exhibits doublets for the isocyanate carbons centered at 135.54 (major) and 135.18 (minor) ppm. The nitrogen atoms for the bridging imido ligands appear downfield at 289.4 ($^1J_{N-H}$ = 55.7 Hz, major) and 296.2 ($^1J_{N-H}$ = 55.7 Hz, minor) ppm. The presence of both the isocyanate and μ-NH ligands was also confirmed by IR spectroscopy, as broad bands for both isomers were observed at 2220 (NCO) and 3564 (μ-NH) cm^{-1}.

To determine whether the two isomers arose from cyclometalation of different methyl groups on the η^5-C_5Me_4H ring, the isomers of **5** were treated with gaseous DCl and the hafnocene dichloride product was analyzed by ^2H NMR spectroscopy (eq 3).



(3)

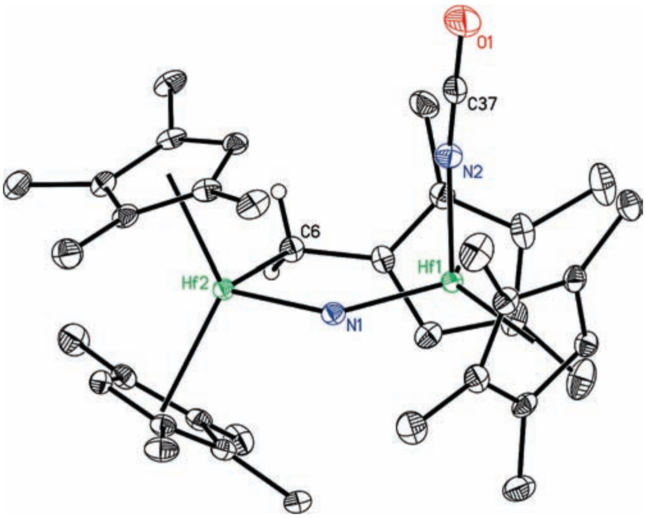


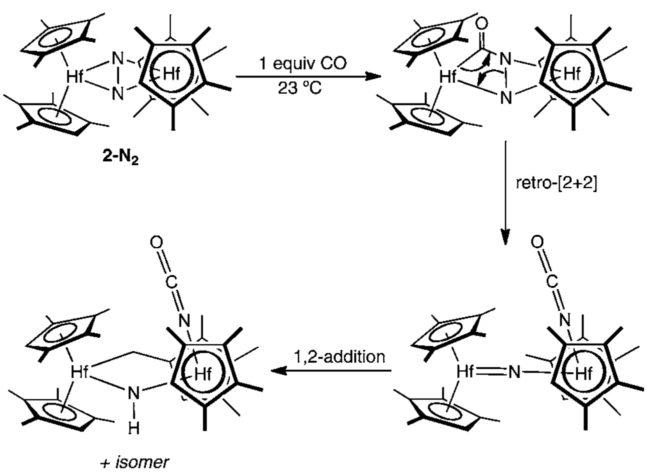
Figure 5. Solid state structure of one of the isomers of **5** shown using 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity, except for those attached to C6.

A single peak centered at 1.82 ppm was observed, indicating that cyclometalation occurred exclusively from the cyclopentadienyl methyl group adjacent to the Cp hydrogen.[23] Therefore, it is most likely that the two isomers arise from cyclometalation of the diastereotopic methyl groups across the dimer (so-called "tuck-over" complexes[47]). It is also possible that the other isomer of **5** is a "tuck-in" complex, where cyclometalation occurs on the same hafnium center rather than across the dimer as observed in the solid state structure.

One of the isomers was also characterized by single-crystal X-ray diffraction. A representation of the solid state structure is presented in Figure 5. The structural data confirm the formation of a hafnocene isocyanate complex with a bridging imido ligand arising from CO-induced N_2 bond cleavage. In addition, the data also establish the formation of a fulvalene-type structure where cyclometalation of a cyclopentadienyl methyl group adjacent to the Cp hydrogen occurred across the dimer and served as the source of the hydrogen for N−H bond formation, likely via 1,2-addition across a μ-nitrido intermediate. The Hf1−N1 and Hf2−N1 distances of 2.034(4) and 2.059(3) Å are elongated for an imido species and more consistent with hafnium−nitrogen single bonds. The Hf1−N1−Hf2 linkage is bent at an angle of 131.47(17)°. This distortion contrasts with the nearly linear angle of 172.5(3)° in the bridging imido formed from addition of 1 equiv of CO to **4** (Scheme 1).[37]

A mechanism for the formation of **5** that is similar to the one proposed for the *ansa*-hafnocene **4-N$_2$**[37] is presented in Scheme 4. One challenge to providing experimental support for such a process is the lack of observables. Much as in the case of **4-N$_2$**, addition of 1.1 equiv of CO to **2-N$_2$** proceeded rapidly without observation of intermediates. The pathway for N_2 cleavage begins with CO insertion into a Hf−N bond followed by a retro-[2 + 2] reaction akin to a β-elimination to generate the terminal isocyanate and a bridging nitrido. Subsequent 1,2-addition in which the carbon of the cyclopentadienyl methyl group is metalated across the dimer yields the final product, **5**. Similar "tuck-over"[47] fulvalene chemistry was observed following the hydrogenation of **2-N$_2$** to form the diazenido hafnocene hydride complex $[(\eta^5\text{-}C_5Me_4H)_2HfH](\mu_2,\eta^2,\eta^2\text{-}N_2H_2)$ (**2-N$_2$H$_4$**). Heating a benzene-d_6 solution of this compound to 65 °C resulted in loss of 1 equiv of H_2 and initially furnished the fulvalene complex where cyclometalation occurred on the same hafnium center. Additional heating at 65 °C resulted in loss of a second equivalent of H_2 and a second cyclometalation event in which both fulvalenes were metalated across the dimer.[23]

Scheme 4. Proposed Mechanism for Ligand-Induced N_2 Bond Cleavage with 1 equiv of CO



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Coupling CO-Induced N$_2$ Cleavage to N−H Bond Formation via Hydrogenation. The observation of ligand-induced N_2 bond cleavage triggered by addition of 1 equiv of CO concomitant with isocyanate formation through a putative bridging nitrido compound raised the possibility that such a species could be intercepted with other reagents. 1,2-Addition of nonpolar molecules such as dihydrogen[20] seemed particularly attractive and, if successful, would couple N_2 cleavage and hydrogenation. One potential challenge with these experiments is the ratio of reagents used, as the reaction of H_2 with the starting dinitrogen compound must be slower than the initial carbonylation and 1,2-addition of H_2 must be faster than the subsequent CO addition step.

The hafnocene dinitrogen complexes were initially targeted for these experiments, as complications from N_2 dissociation were minimized. Exposure of a benzene-d_6 solution of **2-N$_2$** to a 3:1 mixture of CO and H_2 (1 atm total) furnished a new yellow product identified as **2-(μ-NH)(H)(NCO)** (Scheme 4). The reaction commenced immediately upon mixing and required approximately 1 h at 23 °C to reach full conversion. On a practical note, the gases were premixed in a mixing station on a high-vacuum line prior to addition to the hafnocene dinitrogen complex. To ensure that **2-(μ-NH)(H)(NCO)** was not simply a product of the hydrogenation of **5**, a control experiment in which a benzene-d_6 solution of **5** was exposed to 4 atm H_2 was conducted. No change was observed after heating to 100 °C for 24 h, establishing that **2-(μ-NH)(H)(NCO)** was indeed a unique product formed from modified syngas addition to **2-N$_2$**. The observed product likely arises from CO-induced N_2 bond cleavage coupled to N−H bond formation via hydrogenation (eq 4).

The structure of **2-(μ-NH)(H)(NCO)** was unequivocally established by multinuclear NMR spectroscopy (including

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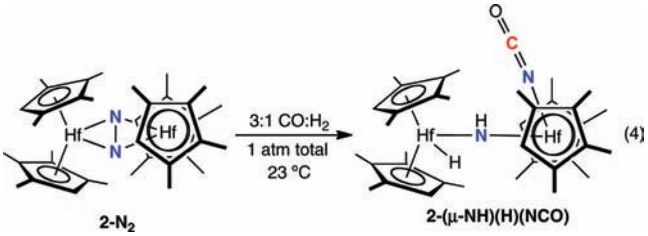
(45) Manriquez, J. M.; McAlister, D. R.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078.

(46) Hanna, T. E.; Keresztes, I.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 1675.

(47) Montalvo, E.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L.; Evans, W. J. *Organometallics* **2010**, *29*, 2104.



(4)

preparation of ^{15}N and ^{13}C isotopologues) and single-crystal X-ray diffraction. A summary of the relevant NMR and IR data for this and related compounds is presented in Table 2. Specifically, the benzene-d_6 ^{15}N NMR spectra of the ^{15}N- and ^{15}N/^{13}C-labeled isotopologues confirm the N−N bond cleavage and N−C bond formation. For the ^{15}N/^{13}C-labeled compound, two doublets were observed at 319.1 ($^1J_{N-H}$ = 45.6 Hz) and 104.3 ($^1J_{N-C}$ = 32.9 Hz) ppm and assigned to the bridging imido and isocyanate nitrogens, respectively (Figure 6). The benzene-d_6 ^{13}C NMR spectrum also exhibits a broad resonance at 135.45 ppm for the terminal NCO ligand, which splits into a sharp doublet upon ^{15}N labeling (Figure 6). The presence of both the μ-NH and NCO groups was confirmed by IR spectroscopy, as bands were observed at 3590 and 2224 cm^{-1} (KBr), respectively. The terminal hafnium hydride was detected by ^{1}H NMR spectroscopy and located downfield at 10.50 ppm. It should be noted that **2-(μ-NH)(H)(NCO)** could only be prepared reproducibly in NMR tubes; attempts to perform the reaction on larger scales resulted in complex mixtures of products.

The solid state structure of **2-(μ-NH)(H)(NCO)** was determined by X-ray diffraction, and a representation of the molecule is presented in Figure 7. Selected metrical parameters are reported in Table 3. The hafnium hydride was located in the difference map, but the imido hydrogen was not. The two hafnocene subunits are canted with respect to each other, forming a dihedral angle of 92.4° between the idealized planes of the two metallocene wedges. The bridging imido ligand is slightly bent, with a Hf1−N2−Hf2 angle of 151.0(2)°. The nitrogen atom is nearly equidistant from the two metal centers with statistically indistinguishable Hf1−N2 and Hf2−N2 distances of 2.042(4) and 2.053(4) Å, respectively. These values are slightly elongated relative to the values of 1.950(4) and 1.987(5) Å reported for the cyclometalated μ-imido *ansa*-hafnocene isocyanate shown in Scheme 1.[37]

CO-triggered dinitrogen cleavage coupled with N−H bond formation by hydrogenation was also explored with the *ansa*-hafnocene complex **4-N_2**. Exposure of a benzene-d_6 solution of the compound to a 3:1 mixture of CO and H_2 at 1 atm total pressure furnished a yellow product identified as **4-(μ-**

Table 2. NMR and IR Spectroscopic Data for the Products of CO-Induced N_2 Bond Cleavage Coupled to N−H Bond Formation by Hydrogenation

compound	δ M−H[a]	δ N−H[a,b]	δ ^{13}C[c]	δ ^{15}N[d]	IR (cm^{-1})[e]
2-(μ-NH)(H)(NCO)	10.50	4.05 (45.6)	135.45 (32.9)	104.3, 319.1	3590, 2224
3-(μ-NH)(H)(NCO)	4.84	6.78 (40.6)	133.65 (30.9)	82.5, 372.0	3610, 2215
4-(μ-NH)(H)(NCO)	9.39	4.66 (40.9)	135.29 (32.9)	N/D,[f] 326.5	3580, 2223
4-(μ-NH)(CCPh)(NCO)	−	5.17 (40.4)	135.52	N/D,[f] 324.1	3577, 2222, 2084[g]
4-(μ-O)(H)(NCO)	9.23	−	136.24 (33.9)	91.4, −	2220,[h] 1560[i]

[a] ^{1}H NMR shift (ppm) in benzene-d_6. [b] The $^1J_{N-H}$ coupling constant (Hz) is reported in parentheses. [c] ^{13}C NMR shift of the M−N*C*O ligand (ppm) recorded in benzene-d_6. The $^1J_{C-N}$ coupling constant (Hz) is reported in parentheses. [d] ^{15}N NMR shifts of the isocyanate ligand (listed first) and μ-NH ligand (listed second). [e] Recorded in KBr. The N−H stretch is listed first, followed by the NCO band, unless otherwise noted. [f] N/D = not determined. [g] IR band for C≡CPh. [h] IR band for the terminal NCO ligand. [i] IR band for Hf−H.

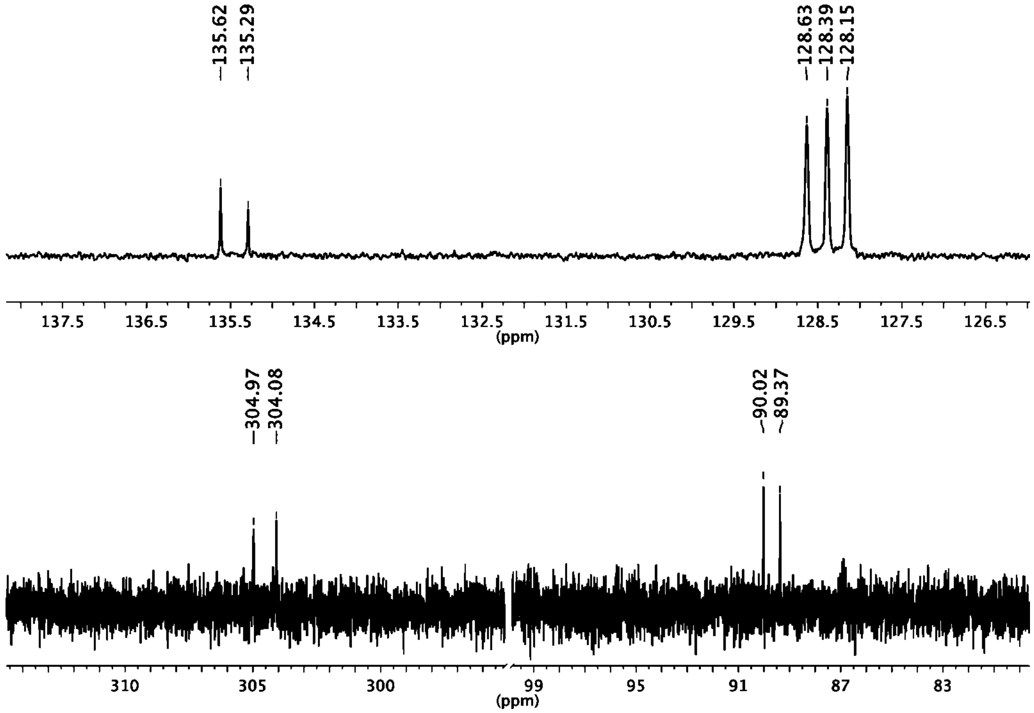


Figure 6. (top) ^{13}C and (bottom) ^{15}N NMR spectra of **2-(μ-NH)(H)(^{15}N^{13}CO)** in benzene-d_6.

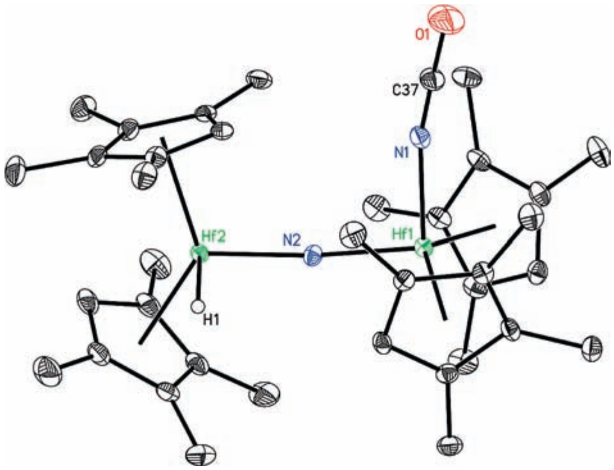


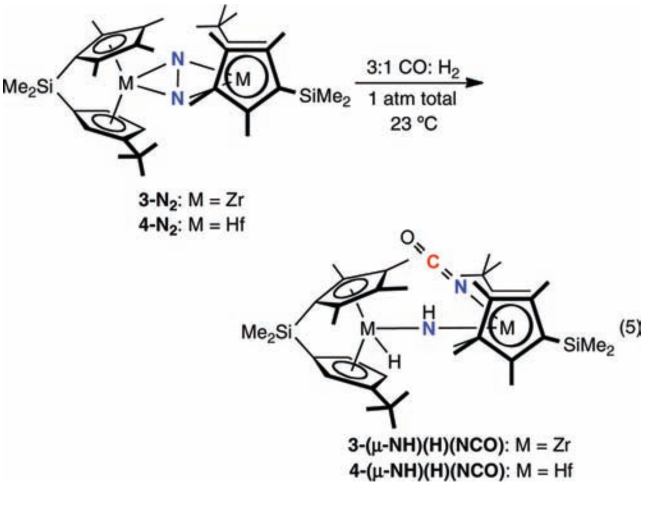
Figure 7. Molecular structure of **2-(*μ*-NH)(H)(NCO)** shown using 30% probability ellipsoids. Hydrogen atoms except for the one in the Hf−H bond have been omitted for clarity. The imido hydrogen was not located.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2-(*μ*-NH)(H)(NCO)**, **4-(*μ*-NH)(H)(NCO)**, and **4-(*μ*-O)(H)(NCO)**

	2-(*μ*-NH)(H)(NCO)	4-(*μ*-NH)(H)(NCO)	4-(*μ*-O)(H)(NCO)
Hf−E[a]	2.053(4) (Hf1) 2.042(4) (Hf2)	2.065(3) (Hf1) 2.048(3) (Hf2)	1.976(2) (Hf1) 1.956(2) (Hf2)
Hf−H	2.06(5)	1.88(3)	1.88(5)
Hf−*N*CO	2.141(4)	2.120(4)	2.093(4)
N═*C*O	1.157(7)	1.114(6)	1.154(6)
N*C*═*O*	1.197(7)	1.255(14)	1.190(6)
Hf−E−Hf[a]	151.0(2)	169.79(18)	147.88(16)
Hf−N−C	167.7(4)	174.1(4)	177.8(4)
N−C−O	178.7(7)	171(2)	179.3(6)

[a] E = *μ*-NH or *μ*-O.

NH)(H)(NCO) arising from CO-induced N_2 bond cleavage and hydrogenation (eq 5).



3-N₂: M = Zr
4-N₂: M = Hf

3-(μ-NH)(H)(NCO): M = Zr
4-(μ-NH)(H)(NCO): M = Hf

Despite the possibility of multiple isomers, only one isomer was observed by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy (see the Supporting Information). The identity of the preferred diastereomer was established by single-crystal X-ray diffraction; its structure is shown in Figure 8, and selected metrical parameters are reported in Table 3. The preferred isomer has both the hafnium hydride and the isocyanate ligand oriented syn to the *tert*-butyl substituents on the cyclopentadienyl rings, and like rings are syn across the dimer with the *tert*-butyl groups directed anti. Bond distances similar to those found in **2-(*μ*-NH)(H)(NCO)** were observed.

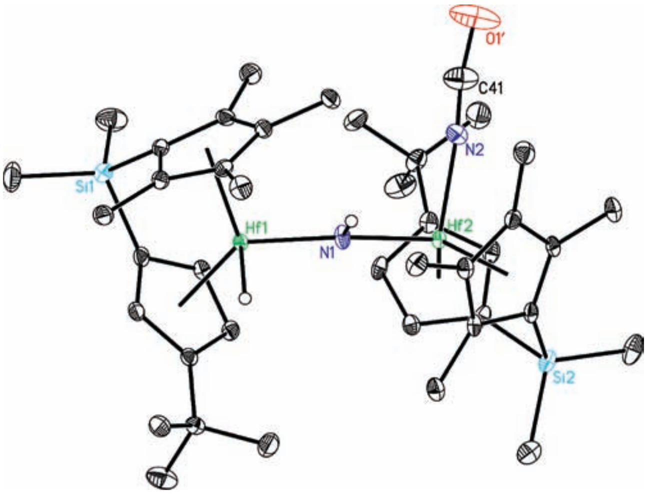


Figure 8. Molecular structure **4-(*μ*-NH)(H)(NCO)** shown using 30% probability ellipsoids. Hydrogen atoms except for those in the Hf−H and N−H bonds have been omitted for clarity. The *S*,*S* enantiomer is shown.

The success of these reactions inspired an exploration of the related chemistry with the zirconium congeners. Successful CO-induced N_2 cleavage coupled to hydrogenation was achieved with the *ansa*-zirconium dinitrogen complex **3-N₂**. Using the same experimental procedure and mixture of gases (3:1 CO/H_2, 1 atm total) afforded the isocyanato hydrido zirconocene *μ*-imido complex **3-(*μ*-NH)(H)(NCO)** as a yellow solid (eq 5). Key spectroscopic data for this compound and its ^{13}C and ^{15}N isotopologues are reported in Table 2. Differentiation between the zirconium hydride and N−H resonances in the ^{1}H NMR spectrum was accomplished by ^{15}N and ^{2}H labeling experiments. Weakly diffracting crystals of **3-(*μ*-NH)(H)(NCO)** were also obtained, allowing the sole isomer formed to be identified as the syn homochiral dimer[48] in which the terminal hydride and isocyanate ligands are positioned over the *tert*-butyl substituents. This is the same diastereomeric preference as in the hafnium congener. A representation of the solid state structure is presented in the Supporting Information.

Attempts to achieve similar chemistry with the compound having the least activated dinitrogen ligand, **1-N₂**, were unsuccessful. Addition of a 3:1 CO/H_2 mixture (1 atm total) resulted in a mixture of products that included the oxamidide complex **1-N₂C₂O₂**, the dicarbonyl compound **1-(CO)₂**, and several other unidentified products. Changing the ratio of the two gases produced little change in the ratio of products, and attempts to separate the products were unsuccessful.

Coupling CO-induced N_2 bond cleavage with N−H bond formation via hydrogenation prompted studies into additional reagents that may undergo 1,2-addition and intercept the putative zirconium or hafnium *μ*-nitrido intermediate. Previous work from Fryzuk's group[29] and our laboratory[23] has demonstrated the rich N_2 functionalization chemistry with terminal alkynes, resulting in N−C and N−H bond formation, respectively. Thus, we sought to trap the putative hafnocene *μ*-nitrido formed after addition of 1 equiv of CO by C−H bond activation. Allowing a frozen benzene-d_6 solution of **4-N₂** containing 10 equiv of PhC≡CH to thaw in the presence of 1 atm CO furnished a single new C_1-symmetric hafnocene product identified as **4-(*μ*-NH)-**

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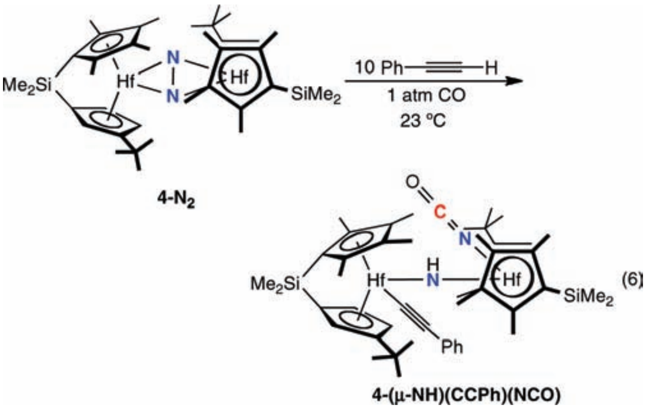
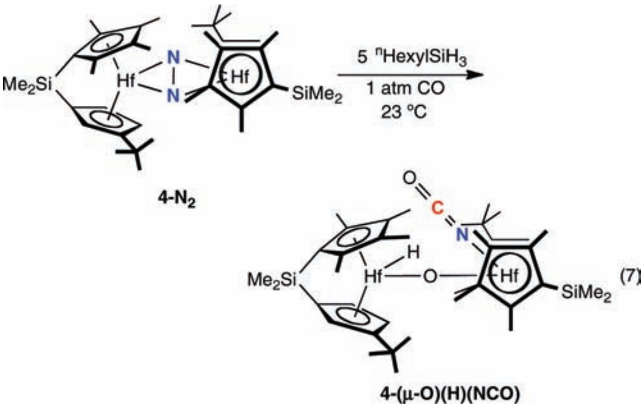
(48) For definitions related to this nomenclature, see ref 46.

(CCPh)(NCO) arising from functionalization of the putative μ-nitrido by 1,2-addition of the acetylene C−H bond (eq 6).



Spectroscopic details for **4-(μ-NH)(CCPh)(NCO)** are reported in Table 2 and in the Supporting Information.

In addition to dihydrogen and terminal alkynes, silanes were also explored as reagents for interception and functionalization of the hafnocene μ-nitrido intermediate. Inspiration for this chemistry was derived from Fryzuk's observation of N_2 functionalization and cleavage in group 4 and 5 dinitrogen chemistry upon addition of $RSiH_3$ reagents.[21,40] Treatment of a benzene-d_6 solution of **4-N_2** with 5 equiv of $^{n}HexylSiH_3$ followed by 1 atm CO furnished, after warming to 23 °C and vigorous shaking for 30 seconds, a yellow solution containing a new C_1-symmetric *ansa*-hafnocene product identified as the μ-oxo hydrido hafnocene isocyanate **4-(μ-O)(H)(NCO)** (eq 7).



This compound was also observed with 1 equiv of silane, although other unidentified products were formed. Notably, **4-(μ-O)(H)(NCO)** was also cleanly prepared from $PhSiH_3$ and $^{n}BuSiH_3$, demonstrating that the silyl fragment was not a component of the final product.

Several pieces of experimental evidence support the formation of a μ-oxide rather than a μ-imide compound. First, the benzene-d_6 ^{1}H NMR spectra of **4-(μ-O)(H)(NCO)** and **4-(μ-NH)(H)(NCO)** are different, with the former exhibiting a Hf−H peak centered at 9.23 ppm and no other signal assignable to a N−H proton. Repeating the experiment with $^{n}HexylSiD_3$ yielded **4-(μ-O)(D)(NCO)**, for which a signal at 9.23 ppm was absent in the ^{1}H NMR spectrum but observable by ^{2}H NMR spectroscopy. Treatment of a benzene-d_6 solution of **4-$^{15}N_2$** with 5 equiv of $^{n}HexylSiH_3$ and 1 atm CO and analysis of the resulting product by ^{15}N NMR spectroscopy revealed only *one* resonance at 91.4 ppm that split into a doublet upon isotopic labeling with ^{13}CO. Both the splitting upon addition of ^{13}CO and the chemical shift demonstrate that this single ^{15}N NMR resonance corresponds to a terminal isocyanate. Additional spectroscopic evidence for formation of this linkage was obtained from ^{13}C NMR experiments and solid state IR spectroscopy and is reported in Table 2. Attempts to collect mass spectral data using either electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI) techniques were unsuccessful.

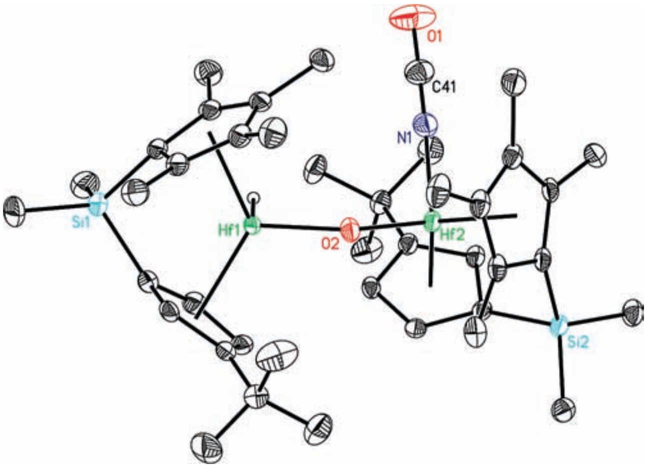


Figure 9. Molecular structure **4-(μ-O)(H)(NCO)** shown using 30% probability ellipsoids. Hydrogen atoms except for the one in the Hf−H bond have been omitted for clarity. The *S*,*S* enantiomer of the molecule is shown.

Single crystals of **4-(μ-O)(H)(NCO)** were obtained from slow evaporation of a benzene solution under an inert atmosphere, and a representation of the solid state structure is presented in Figure 9. Data were collected on two independently obtained samples, and unfortunately, both suffered from the same crystallographic disorder. A large (~10 e/Å^3) difference Fourier peak was located near (0.9 Å from) the Hf1 atom, consistent with whole-molecule disorder. All of the other atoms were invisible, and the minor hafnium component constituted one-ninth of the mixture. Despite these complications, the X-ray data establish a bimetallic structure with a terminal isocyanate and a bridging oxo ligand. Unlike the one in **4-(μ-NH)(H)(NCO)**, the hydride ligand is oriented away from the Cp *tert*-butyl substituent. The Hf1−O2 and Hf2−O2 distances of 1.976(2) and 1.956(2) Å are contracted relative to the corresponding lengths of 2.065(3) and 2.048(3) Å found in the related μ-imide **4-(μ-NH)(H)(NCO)**. Other selected bond distances and angles are reported in Table 3 and are comparable to those in the structurally characterized μ-imide compounds.

Because ^{15}N NMR spectroscopy provided only negative evidence for formation of **4-(μ-O)(H)(NCO)** (i.e., the absence of a second signal) and definitively distinguishing μ-NH from μ-O by X-ray diffraction is tenuous, additional chemical evidence supporting the proposed structure was sought. One significant difference between **4-(μ-O)(H)(NCO)** and **4-(μ-NH)(H)(NCO)** would be the products of protonolysis. For **4-(μ-NH)(H)(NCO)** and the other μ-NH compounds prepared in this work, the expected protonolysis products would be HNCO and NH_3. In principle, protonation of **4-(μ-O)(H)(NCO)** should yield no ammonia, although the aqueous colorimetric (phenol−hypochlorite) method for NH_3 detection[49] would likely result in the known hydrolysis of HNCO to yield quantities of the

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(49) Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971.

Table 4. Amount of Ammonia Detected following Treatment with 20 equiv of HCl and Aqueous Digestion (NH_3 Was Quantified by the Method Described in Ref 49)

compound	% NH_3[a]
2-(μ-NH)(H)(NCO)	147.4
3-(μ-NH)(H)(NCO)	175.2
4-(μ-NH)(H)(NCO)	166.8
4-(μ-O)(H)(NCO)	71.8

[a] The percent yields are reported with respect to the μ-NH ligand. Thus, yields in excess of 100% take into account the ammonia produced from the hydrolysis of HNCO.

amine.[50] To address this issue, several compounds prepared in this work were treated with an excess (~20 equiv) of anhydrous HCl, and the resulting ammonia was measured.[49] The results of these experiments are presented in Table 4.

The percentage of ammonia reported in Table 4 is with respect to 1 equiv of NH_3, assuming that the μ-NH ligand is the only source of ammonia. For the compounds containing both an imide and a terminal isocyanate ligand, the excess ammonia generated from hydrolysis of HNCO is reflected in the value. For all three imide compounds, values in vast excess of 100% were measured, establishing that a significant amount of NH_3 resulted from HNCO hydrolysis. Notably, the yield of ammonia detected from protonolysis of **4-(μ-O)(H)(NCO)** was only 71.8%, which is significantly lower than those obtained from the compounds with μ-NH ligands and on par with the amount of NH_3 observed from the hydrolysis of HNCO. Thus, the aqueous digestion experiments support the lack of a second nitrogen atom and hence of a bridging imide in **4-(μ-O)(H)(NCO)**.

Because the hydrolysis of HNCO produces ammonia and thereby complicates differentiation of the μ-O versus μ-NH possibilities in **4-(μ-O)(H)(NCO)**, degradation experiments were also conducted under rigorously anhydrous conditions. In a typical experiment, excess anhydrous HCl was added to the hafnocene of interest, and the volatiles were removed in vacuo to eliminate all of the free HNCO byproduct. The resulting solids were analyzed by the colorimetric method for ammonia detection. Using this procedure, the imido complex **4-(μ-NH)(H)(NCO)** yielded 75.7% of the ammonia expected on the basis of one μ-NH ligand, whereas **4-(μ-O)(H)(NCO)** produced only 8.0%. Thus, both the aqueous and anhydrous protonolysis experiments support a μ-O rather than a μ-NH ligand in **4-(μ-O)(H)(NCO)**.

With the identity of **4-(μ-O)(H)(NCO)** confirmed, definitively establishing CO as the source of the O atom was explored. The reproducibility of the reaction with different silanes, the high conversions, and the presence of a hafnium hydride are all inconsistent with adventitious water as the source of the oxygen atom. If CO cleavage is the source of the oxygen atom, what then are the fates of the carbon and nitrogen atoms following CO deoxygenation? Monitoring the reaction of CO and $^{n}HexylSiH_3$ with **4-N$_2$** by ^{1}H NMR and IR spectroscopies immediately following addition established the formation of $^{n}HexylSiH_2CN$ at short reaction times. The identity of this product was confirmed by independent synthesis.[51] Over the course of minutes at 23 °C, the resonances for $^{n}HexylSiH_2CN$ disappeared and no new silane resonances were observed. We note that excess $^{n}HexylSiH_3$ was present during the transformation, and thus, detection of this compound when formed in such small quantities was challenging. Analysis of the product mixture by IR spectroscopy after consumption of the $^{n}HexylSiH_2CN$ revealed cyanide bands, suggesting ligand redistribution to form $^{n}HexylSi(CN)_3$ and $^{n}HexylSiH_3$. The experimental data are therefore consistent with CO deoxygenation and functionalization of a nitrogen atom to form a cyanosilane that is removed from the coordination sphere of the hafnium.

Concluding Remarks

The scope of CO-induced N_2 cleavage in zirconocene and hafnocene complexes with side-on bound dinitrogen ligands has been explored. The transformation was observed for each compound studied, and when 2 equiv of CO was added, N_2 cleavage with concomitant N–C and C–C bond formation occurred. Treatment of the methylated hafnocene dinitrogen complex $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2\text{-}N_2)$ with 1 equiv of CO resulted in N_2 cleavage coupled to N–H bond formation via C–H activation and yielded a bimetallic hafnocene complex with a terminal isocyanate and bridging fulvalene and imido ligands. Mechanistic considerations suggested the formation of a putative μ-nitrido hafnocene intermediate that was intercepted with various nonpolar reagents via 1,2-addition. In this manner, CO-induced N_2 cleavage was coupled to N–H bond formation via hydrogenation and C–H activation of terminal alkynes. Attempts to replicate this chemistry with primary silanes resulted in a different outcome, furnishing an isocyanato hydrido hafnocene oxo complex consistent with CO and N_2 cleavage and demonstrating that an *ansa*-hafnocene complex is capable of cleaving the diatomics with the two strongest bonds in chemistry.

Experimental Section[52]

Preparation of $((\eta^5\text{-}C_5Me_4H)_2Zr)_2(N_2C_2O_2)$ (1-N$_2$C$_2$O$_2$). In a drybox, a J. Young NMR tube was charged with 0.020 g (0.027 mmol) of **1-N$_2$**,[22] and ~0.5 mL of benzene-d_6 was added. On a high-vacuum line, the tube was submerged in liquid nitrogen and degassed, after which 1 atm CO was admitted at −196 °C. The contents of the tube were thawed, and the resulting reaction was monitored over the course of several hours. Initially, the starting dinitrogen compound was converted to a roughly 1:1 mixture of **1-N$_2$C$_2$O$_2$** and $[(\eta^5\text{-}C_5Me_4H)_2Zr(CO)]_2(\mu_2\text{-}N_2)$. Over the course of several hours, $[(\eta^5\text{-}C_5Me_4H)_2Zr(CO)]_2(\mu_2\text{-}N_2)$ was fully converted to **1-(CO)$_2$**,[44] affording a final **1-N$_2$C$_2$O$_2$/1-(CO)$_2$** ratio of approximately 3:1 ^{1}H NMR (benzene-d_6): δ 1.87 (s, 12H, Cp*Me*$_4$H), 1.88 (s, 12H, Cp*Me*$_4$H), 2.02 (s, 12H, Cp*Me*$_4$H), 2.07 (s, 12H, Cp*Me*$_4$H), 5.76 (s, 4H, CpMe$_4$*H*). $\{^{1}H\}^{13}C$ NMR (benzene-d_6): δ 12.05 (Cp*Me*), 12.36 (Cp*Me*), 13.25 (Cp*Me*), 13.42 (Cp*Me*), 111.66, 119.40, 119.94, 124.62, 124.65 (*Cp*), 162.89 ($N_2C_2O_2$). ^{15}N NMR (benzene-d_6): δ 400.4 ($^{15}N_2C_2O_2$) ($^{1}J_{C-N}$, $^{2}J_{C-N} = 3.7$ Hz (average)). IR (KBr) ν (cm^{-1}): 1590 (C=N).

Preparation of $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(N_2C_2O_2)$ (2-N$_2$C$_2$O$_2$). In a drybox, a thick-walled glass vessel was charged with 0.150 g (0.172 mmol) of **2-N$_2$**[30] dissolved in ~20 mL of toluene. On a high-vacuum line, the vessel was degassed and 1 atm CO was admitted at −196 °C to give a total pressure of 4 atm at 23 °C. The vessel was thawed and its contents stirred for 2 h, after which time excess gas and solvent were removed in vacuo. In a drybox, the resulting burgundy oil was washed with cold pentane, furnishing a yellow solid. This solid was dissolved in toluene and recrystallized at −35 °C, affording pale-yellow crystals of the desired product **2-N$_2$C$_2$O$_2$** in 75% yield. Anal. Calcd for $C_{38}H_{52}N_2O_2Hf_2$: C, 49.30; H, 5.66; N, 3.03. Found: C, 49.45; H, 5.75; N, 2.92. ^{1}H NMR (benzene-d_6): δ 1.92 (s, 24H, Cp*Me*$_4$H (2 coincident environments)), 2.02 (s, 12H,

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(52) General considerations and additional experimental details are reported in the Supporting Information.

Cp*Me*$_4$H), 2.07 (s, 12H, Cp*Me*$_4$H), 5.73 (s, 4H, CpMe$_4$*H*). {^{1}H}^{13}C NMR (benzene-d_6): δ 11.99 (Cp*Me*), 12.34 (Cp*Me*), 13.17 (Cp*Me*), 13.26 (Cp*Me*), 111.34, 117.89, 118.32, 123.65, 123.68 (*Cp*), 160.2 (N$_2$*C*$_2$O$_2$). ^{15}N NMR (benzene-d_6): δ 376.2 ($^{15}N_2C_2O_2$) ($^1J_{\mathrm{C-N}}$, $^2J_{\mathrm{C-N}}$ = 3.9 Hz (average)). IR (KBr) ν (cm^{-1}): 1593 (C=N), 1560 (^{13}C=N).

Preparation of ([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Zr)$_2$(N$_2$C$_2$O$_2$) (3-N$_2$C$_2$O$_2$-*C$_1$*; *C*$_1$-Symmetric Isomer). In a drybox, a thick-walled glass vessel was charged with 0.100 g (0.124 mmol) of **3-N$_2$**[46] dissolved in ~10 mL of toluene. On a high-vacuum line, the vessel was degassed and 1 atm CO was admitted at −196 °C. The contents of the vessel were thawed and stirred for 2 h, at which time excess gas and solvent were removed in vacuo. In a drybox, the resulting deep-red oil was washed with cold pentane to remove the small amounts of the byproduct zirconocene dicarbonyl, **3-(CO)$_2$**.[46] The remaining yellow solid was dissolved in diethyl ether and recrystallized at −35 °C, affording pale-yellow crystals of **3-N$_2$C$_2$O$_2$-*C$_1$*** in 42% yield. Anal. Calcd for $C_{42}H_{60}O_2N_2Si_2Zr_2$: C, 58.41; H, 7.00; N, 3.24. Found: C, 58.08; H, 7.10; N, 3.08. ^{1}H NMR (benzene-d_6): δ 0.47 (s, 3H, Si*Me*$_2$), 0.48 (s, 3H, Si*Me*$_2$), 0.65 (s, 3H, Si*Me*$_2$), 0.66 (s, 3H, Si*Me*$_2$), 1.32 (s, 9H, C$_5$H$_3$C*Me*$_3$), 1.41 (s, 9H, C$_5$H$_3$C*Me*$_3$), 1.90 (s, 3H, C$_5$*Me*$_4$), 1.96 (s, 3H, C$_5$*Me*$_4$), 2.02 (s, 3H, C$_5$*Me*$_4$), 2.04 (s, 3H, C$_5$*Me*$_4$), 2.07 (s, 3H, C$_5$*Me*$_4$), 2.10 (s, 3H, C$_5$*Me*$_4$), 2.19 (s, 3H, C$_5$*Me*$_4$), 2.21 (s, 3H, C$_5$*Me*$_4$), 5.75 (m, 1H, C$_5$*H*$_3$CMe$_3$), 5.76 (m, 1H, C$_5$*H*$_3$CMe$_3$), 5.92 (m, 1H, C$_5$*H*$_3$CMe$_3$), 5.98 (m, 1H, C$_5$*H*$_3$CMe$_3$), 6.60 (m, 1H, C$_5$*H*$_3$CMe$_3$), 6.64 (m, 1H, C$_5$*H*$_3$CMe$_3$). {^{1}H}^{13}C NMR (benzene-d_6): δ −0.93 (Si*Me*$_2$), −0.87 (Si*Me*$_2$), 1.31 (Si*Me*$_2$), 1.44 (Si*Me*$_2$), 11.41 (Cp*Me*), 11.60 (Cp*Me*), 11.81 (Cp*Me*), 12.22 (Cp*Me*), 14.61 (Cp*Me*), 15.01 (Cp*Me*), 15.18 (Cp*Me*), 15.68 (Cp*Me*), 31.48 (C*Me*$_3$), 31.53 (C*Me*$_3$), 33.53 (*C*Me$_3$), 33.72 (*C*Me$_3$), 102.26, 104.50, 109.96, 111.34, 113.39, 114.01, 115.06, 118.77, 119.36, 120.84, 122.28, 126.03, 126.97, 129.54, 129.66, 132.48, 133.47, 134.41, 152.45, 153.23 (*Cp*), 162.76 (N$_2$*C*$_2$O$_2$), 164.07 (N$_2$*C*$_2$O$_2$). ^{15}N NMR (benzene-d_6): δ 392.4 ($^{15}N_2C_2O_2$), 396.5 ($^{15}N_2C_2O_2$) ($^1J_{\mathrm{C-C}} = 60.9$ Hz, $^1J_{\mathrm{C-N}} = 4.0$ Hz, $^2J_{\mathrm{C-N}} = 4.0$ Hz). IR (KBr) ν (cm^{-1}): 1574 (C=N), 1535 (^{13}C=N).

Preparation of ((η^5-C$_5$Me$_4$H)$_2$Hf)((CH$_2$-η^5-C$_5$Me$_3$H)(η^5-C$_5$Me$_4$H)Hf)(μ-NH)(NCO) (5). In a drybox, a J. Young NMR tube was charged with 0.015 g (0.016 mmol) of **2-N$_2$** and ~0.5 mL of benzene-d_6. The contents of the tube were frozen, and the tube was evacuated. To an attached calibrated gas bulb, 1.1 equiv (25 Torr, 13.1 mL) of CO was admitted. The contents of the tube were thawed, and the CO was slowly diffused into the solution over 16 h at room temperature, during which time a color change from purple to yellow was observed. ^{1}H NMR spectroscopy established complete conversion to two isomers of **5**. This process was repeated in several independent NMR tubes, after which the products were combined and the solvent was removed in vacuo. The resulting oil was dissolved in toluene, and single crystals of a single isomer were obtained via slow evaporation of the solvent. The reaction was reproducible with **2-^{15}N$_2$** and ^{13}CO, enabling the synthesis and characterization of various ^{15}N and ^{13}C isotopologue combinations of **5**. ^{1}H NMR (benzene-d_6) (mixture of two isomers): δ 1.55 (s, 3H, Cp*Me*$_4$H), 1.56 (s, 3H, Cp*Me*$_4$H), 1.61 (s, 3H, Cp*Me*$_4$H), 1.62 (s, 3H, Cp*Me*$_4$H), 1.68 (s, 3H, Cp*Me*$_4$H), 1.69 (s, 3H, Cp*Me*$_4$H), 1.70 (s, 3H, Cp*Me*$_4$H), 1.71 (s, 3H, Cp*Me*$_4$H), 1.73 (two coincident, m, 2H, Hf−C*H*$_2$), 1.74 (s, 3H, Cp*Me*$_4$H), 1.75 (s, 3H, Cp*Me*$_4$H), 1.77 (s, 3H, Cp*Me*$_4$H), 1.78 (s, 3H, Cp*Me*$_4$H), 1.79 (s, 3H, Cp*Me*$_4$H), 1.82 (s, 3H, Cp*Me*$_4$H), 1.83 (three coincident, s, 9H, Cp*Me*$_4$H), 1.86 (s, 3H, Cp*Me*$_4$H), 1.87 (s, 3H, Cp*Me*$_4$H), 1.88 (two coincident, s, 6H, Cp*Me*$_4$H), 1.92 (s, 3H, Cp*Me*$_4$H), 1.95 (s, 3H, Cp*Me*$_4$H), 1.97 (s, 3H, Cp*Me*$_4$H), 1.99 (s, 3H, Cp*Me*$_4$H), 2.00 (s, 3H, Cp*Me*$_4$H), 2.02 (s, 3H, Cp*Me*$_4$H), 2.06 (s, 3H, Cp*Me*$_4$H), 2.07 (s, 3H, Cp*Me*$_4$H), 2.10 (s, 3H, Cp*Me*$_4$H), 2.21 (s, 3H, Cp*Me*$_4$H), 2.40 (s, 3H, Cp*Me*$_4$H), 2.56 (two coincident, m, 4H, Hf−C*H*$_2$), 4.60 (s, 1H, CpMe$_4$*H*), 5.07 (s, 1H, CpMe$_4$*H*), 5.10 (s, 1H, CpMe$_4$*H*), 5.17 (s, 1H, CpMe$_4$*H*), 5.19 (two coincident, s, 2H, CpMe$_4$*H*), 5.68 (s, 1H, CpMe$_4$*H*), 5.69 (br s, 1H, μ-N*H* (major)), 5.73 (br s, 1H, μ-N*H* (minor)), 6.19 (s, 1H, CpMe$_4$*H*). ^{13}C NMR (benzene-d_6): δ 11.21, 11.52, 11.70, 12.03, 12.16, 12.20, 12.24, 12.32, 12.45, 12.69, 12.85, 12.92, 13.02, 13.19, 13.29, 13.36, 13.41, 13.47, 13.59, 13.66, 13.69, 13.76, 14.04, 14.21, 14.45, 14.55, 14.59, 15.36, 15.69, 15.79 (Cp*Me*), 23.05 (Hf-*C*H$_2$ (major)), 36.65 (Hf-*C*H$_2$ (minor)), 101.66, 101.73, 107.09, 107.14, 108.07, 108.46, 108.58, 108.99, 109.14, 109.24, 109.72, 109.85, 110.96, 111.04, 111.47, 112.16, 112.35, 112.51, 112.76, 113.57, 113.83, 114.00, 117.12, 118.13, 118.77, 118.97, 119.35, 119.52, 119.81, 112.13, 120.61, 120.90, 121.93, 122.50, 124.14, 124.32, 126.02, 130.16, 131.93, 136.58 (*Cp*), 135.18 (N*C*O, $^1J_{\mathrm{N-C}} = 32.6$ Hz (minor)), 135.54 (N*C*O, $^1J_{\mathrm{N-C}} = 32.4$ Hz (major)). ^{15}N NMR (benzene-d_6): δ 289.4 (μ-*N*H) ($^1J_{\mathrm{N-H}} = 55.7$ Hz) (major), 296.2 (μ-*N*H) ($^1J_{\mathrm{N-H}} = 55.7$ Hz) (minor), 86.8 (*N*CO) (major), 84.2 (*N*CO) (minor). IR (KBr) ν (cm^{-1}): 2220 (NCO), 3564 (N−H).

Preparation of ((η^5-C$_5$Me$_4$H)$_2$Hf)$_2$(μ-NH)(H)(NCO) (2-(μ-NH)(H)(NCO)). In a drybox, a J. Young NMR tube was charged with 0.015 g (0.016 mmol) of **2-N$_2$** and ~0.5 mL of benzene-d_6. The contents of the tube were frozen, and the tube was evacuated. A mixture of CO and H$_2$ ($P_{\mathrm{CO}}/P_{\mathrm{H_2}} = 3{:}1$, ~1 atm total) was admitted to the tube at liquid nitrogen temperature. The contents of the tube were thawed with vigorous shaking, and a color change to yellow was observed over the course of 30 s at room temperature. Monitoring the reaction by ^{1}H NMR spectroscopy established the complete conversion to **2-(μ-NH)(H)(NCO)** after 1 h. This process was repeated in several independent NMR tubes, after which the products were combined and the solvent was removed in vacuo. The resulting oil was washed with pentane and furnished an analytically pure pale-yellow solid identified as **2-(μ-NH)(H)(NCO)**. The reaction was reproducible with **2-^{15}N$_2$** and ^{13}CO, enabling the synthesis and characterization of various ^{15}N and ^{13}C isotopologue combinations. Anal. Calcd for $C_{37}H_{54}O_1N_2Hf_2$: C, 49.38; H, 6.05; N, 3.11. Found: C, 49.66; H, 5.99; N, 2.89. ^{1}H NMR (benzene-d_6): δ 1.70 (s, 3H, Cp*Me*$_4$H), 1.73 (s, 3H, Cp*Me*$_4$H), 1.80 (s, 3H, Cp*Me*$_4$H), 1.83 (s, 3H, Cp*Me*$_4$H), 1.84 (s, 3H, Cp*Me*$_4$H), 1.87 (s, 3H, Cp*Me*$_4$H), 1.88 (s, 3H, Cp*Me*$_4$H), 1.95 (s, 3H, Cp*Me*$_4$H), 1.99 (s, 3H, Cp*Me*$_4$H), 2.00 (s, 3H, Cp*Me*$_4$H), 2.05 (s, 3H, Cp*Me*$_4$H), 2.06 (s, 3H, Cp*Me*$_4$H), 2.10 (s, 3H, Cp*Me*$_4$H), 2.27 (s, 3H, Cp*Me*$_4$H), 2.33 (s, 3H, Cp*Me*$_4$H), 2.41 (s, 3H, Cp*Me*$_4$H), 4.05 (s, 1H, μ-N*H*), 5.16 (s, 1H, CpMe$_4$*H*), 5.23 (s, 1H, CpMe$_4$*H*), 5.30 (s, 1H, CpMe$_4$*H*), 6.08 (s, 1H, CpMe$_4$*H*), 10.50 (s, 1H, Hf*H*). ^{13}C NMR (benzene-d_6): δ 11.80, 11.90, 12.06, 12.23, 12.97, 13.10, 13.40, 13.60, 13.86, 14.16, 14.39, 14.47, 14.61, 14.71, 14.73, 14.91 (Cp*Me*), 108.73, 110.32, 110.86, 112.81, 113.18, 113.40, 114.26, 114.66, 116.09, 116.19, 117.38, 118.48, 120.33, 120.57, 120.78, 121.09, 121.18, 121.82, 125.25, 126.03 (*Cp*), 135.45 (N*C*O). ^{15}N NMR (benzene-d_6): δ 319.1 (μ-*N*H) ($^1J_{\mathrm{N-H}} = 45.6$ Hz), 104.3 (*N*CO) ($^1J_{\mathrm{N-C}} = 32.9$ Hz). IR (KBr) ν (cm^{-1}): 2224 (NCO), 3590 (N−H).

Preparation of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)Hf]$_2$(μ-NH)(CCPh)(NCO) (4-(μ-NH)(CCPh)(NCO)). In a drybox, a J. Young NMR tube was charged with 0.010 g (0.010 mmol) of **4-N$_2$** and ~0.5 mL of benzene-d_6. The contents of the tube were frozen in a cold well, and phenylacetylene (10 μL, 0.091 mmol) was layered on top of the frozen solution. The tube was sealed and quickly transferred to a high-vacuum line, where the headspace of the tube was degassed. CO (1 atm) was admitted to the tube at liquid nitrogen temperature. The contents of the tube were thawed with vigorous shaking, and a color change to light-orange was observed over the course of 30 s at ambient temperature. Monitoring the reaction by ^{1}H NMR spectroscopy established the complete conversion to **4-(μ-NH)(CCPh)(NCO)**. This process was repeated in several independent NMR tubes, after which the products were combined and the solvent and excess phenylacetylene were removed in vacuo. The resulting oil was washed with pentane and furnished analytically pure **4-(μ-NH)(CCPh)(NCO)**. The reaction was also conducted with **4-^{15}N$_2$** and ^{13}CO, enabling the synthesis and characterization of various ^{15}N and ^{13}C isotopologues. ^{1}H NMR (benzene-d_6): δ 0.49 (s, 3H, Si*Me*$_2$), 0.51 (s, 3H, Si*Me*$_2$), 0.58 (s, 3H, Si*Me*$_2$), 0.62 (s, 3H, Si*Me*$_2$), 1.45 (s, 9H, C$_5$H$_3$C*Me*$_3$), 1.63 (s, 9H, $C_5H_3CMe_3$), 1.84 (s, 3H, C_5Me_4), 1.94 (s, 3H, C_5Me_4), 1.95 (s, 3H, C_5Me_4), 1.96 (s, 3H, C_5Me_4), 2.00 (s, 3H, C_5Me_4), 2.07 (s, 3H, C_5Me_4), 2.16 (s, 3H, C_5Me_4), 2.27 (s, 3H, C_5Me_4), 5.17 (s, 1H, μ-N*H*) 5.46 (m, 1H, $C_5H_3CMe_3$), 5.54 (m, 1H, $C_5H_3CMe_3$), 6.03 (m, 1H, $C_5H_3CMe_3$), 6.18 (m, 1H, $C_5H_3CMe_3$), 6.93 (m, 1H, $C_5H_3CMe_3$), 6.96 (m, 1H, $C_5H_3CMe_3$), 7.11−7.22 (m, 1H, *Ph*), 7.54−7.68 (m, 4H, *Ph*). $\{^1H\}^{13}C$ NMR (benzene-d_6): δ −0.17 ($SiMe_2$), −0.05 ($SiMe_2$), 0.18 ($SiMe_2$), 0.22 ($SiMe_2$), 11.32 (Cp*Me*), 12.00 (Cp*Me*), 12.07 (Cp*Me*), 13.65 (Cp*Me*), 14.24 (Cp*Me*), 15.00 (Cp*Me*), 15.24 (Cp*Me*), 15.31 (Cp*Me*), 31.41 (CMe_3), 31.85 (CMe_3), 33.66 (CMe_3), 33.80 (CMe_3), 98.71, 99.82 (*CC*Ph), 105.30, 107.70, 108.12, 108.23, 108.63, 111.96, 112.67, 116.39, 116.63, 120.90, 121.71, 123.13, 126.33, 127.27, 127.39, 127.53, 128.68, 128.98, 129.01, 130.76, 131.23, 132.33, 151.16, 151.94 (*Cp* and *Ph*), 135.52 (N*C*O). IR (KBr) ν (cm^{-1}): 2084 (CCPh), 2222 (NCO), 3577 (N−H).

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Supporting Information Available: General experimental considerations and additional procedures; crystallographic data for **2-$N_2C_2O_2$**, **2-(μ-NH)(H)(NCO), 3-(μ-NH)(H)(NCO)**, **4-(μ-NH)(H)(NCO)**, **4-(μ-O)(H)(NCO)**, and one isomer of **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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