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Di- and Tetrametallic Hafnocene Oxamidides Prepared from CO-Induced N_2 Bond Cleavage and Thermal Rearrangement to Hafnocene Cyanide Derivatives

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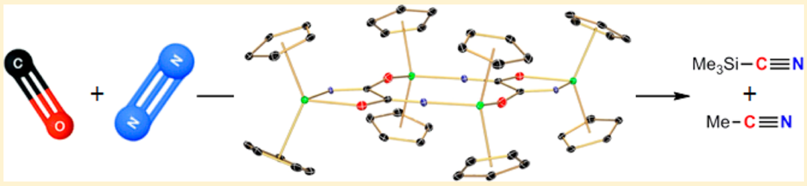
Supporting Information



ABSTRACT: Carbonylation of the hafnocene dinitrogen complex $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2:\eta^2\text{-}N_2)$ with 4 atm of carbon monoxide yielded the tetrametallic hafnocene oxamidide complex $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$, a new structural motif arising from CO-induced N_2 cleavage. The more commonly observed dimeric hafnocene oxamidide $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(N_2C_2O_2)$ was observed by multinuclear NMR spectroscopy when the carbonylation was performed at lower (~1 atm) CO pressure. Over the course of 1 h at 23 °C, the dimeric hafnocene oxamidide undergoes dimerization to the tetrametallic compound, establishing its intermediacy for synthesis of the latter. Additional functionalization of the hafnium−nitrogen bonds in the tetrametallic complex was accomplished by cycloaddition of ^{t}BuNCO or 1,2-addition of $CySiH_3$. The former example maintains a tetrametallic hafnocene where only two of the four Hf−N bonds have undergone [C═O] cycloaddition of the heterocumulene. In contrast, the primary silane yielded a dimeric hafnocene product where all of the hafnium−nitrogen linkages have undergone 1,2-addition. Thermolysis of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$ at 110 °C provided a route to a new μ-oxo hafnocene complex with both terminal isocyanate and cyanide ligands. This process is general among hafnocene oxamidides and provides a route to rare hafnium cyanide complexes that undergo preferential [CN] rather than [NCO] group transfer.

■ INTRODUCTION

The synthesis of nitrogen-containing organic molecules from dinitrogen is a long-standing challenge owing to the kinetic and thermodynamic stability of the N_2 molecule.[1] Biological[2] and industrial nitrogen fixation[3,4] produces ammonia on an enormous scale, and the resulting NH_3 is used to prepare most synthetic nitrogen compounds.[5] Methods that directly assemble nitrogen−carbon bonds from N_2 are attractive to circumvent the energy requirements for ammonia synthesis.[6−8]

Ligand-induced dinitrogen cleavage, where an incoming reagent simultaneously supplies reducing equivalents and forms a new nitrogen-element bond, has evolved into an effective strategy for elaboration of N_2. This approach is particularly useful with early-transition-metal compounds that do not have the necessary reducing equivalents to promote N≡N scission. Fryzuk and co-workers have pioneered this strategy in tantalum dinitrogen chemistry[9] and have demonstrated that addition of alanes,[10] silanes,[11] boranes,[12] and zirconocene hydrides[13] induce N−N cleavage with concomitant formation of new nitrogen-element bonds. Our laboratory has extended this approach to group 4 metallocene dinitrogen compounds where the reduced zirconium or hafnium centers supply only four of the six electrons required for N_2 splitting.[14,15] It is likely that ligand-induced N_2 cleavage plays a role in the liberation of ammonia from hydrogenation of a strongly activated zirconocene dinitrogen complex.[16,17] This approach is in contrast with the seminal work of van Tamelen and co-workers, where reduction of titanocene chloride with excess magnesium powder followed by treatment with ketones or acid chlorides yields amines or nitriles, respectively.[18] It was postulated that the combination of the transition metal and the alkaline-earth-metal reductant supplied the necessary electrons to promote N_2 cleavage.[19,20]

Carbon monoxide induced N_2 cleavage has emerged as a powerful method for N_2 cleavage, with concomitant assembly of N−C and C−C bonds.[21−23] First observed by Sobota in a $TiCl_4$/Mg mixture,[24] our laboratory has since developed this reaction as a general transformation among zirconocene and hafnocene compounds with strongly activated N_2 ligands[25] and as a method to synthesize substituted oxamides.[26] CO-induced dinitrogen cleavage has also been applied to the synthesis of a hafnocene μ-formamidide ($[NC(H)O]^{2-}$) ligand and ultimately free formamide following silylation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2:\eta^2\text{-}N_2)$ (**1-N₂**).[27] Experimental[18,28] and computational investigations[29] into the mechanism of oxamidide formation from carbonylation of zirconocene and hafnocene dinitrogen compounds support the formation of intermediate

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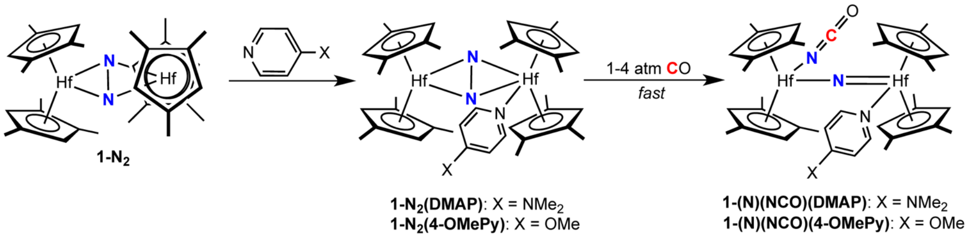
Scheme 1. Synthesis of Pyridine-Stabilized Hafnocene μ-Nitrido Complexes by CO-Induced N_2 Bond Cleavage

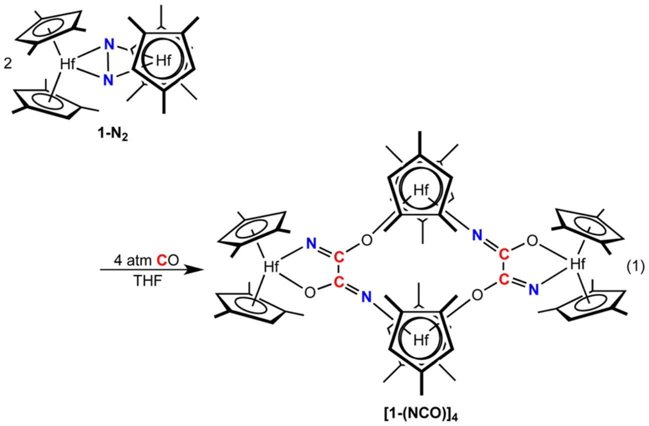


μ-nitrido complexes, and pyridine-stabilized examples have recently been isolated and crystallographically characterized (Scheme 1).[30]

Here we describe additional studies into the base-free carbonylation of **1-N$_2$** and report the isolation and characterization of an unusual tetrametallic oxamidide compound prepared from dinitrogen cleavage. The cyclo- and 1,2-addition reactivity of this species is reported and compared to more well established dinuclear hafnocene oxamidides. A new thermally induced deoxygenation and isomerization of hafnocene oxamidides has also been discovered and applied to the synthesis of rare hafnium cyanide complexes and ultimately organic nitriles.

RESULTS AND DISCUSSION

Carbonylation of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(μ_2,η^2:η^2-N_2). Exposure of a THF solution of **1-N$_2$** to 4 atm of carbon monoxide followed by recrystallization at −35 °C furnished yellow crystals identified as the tetrametallic hafnocene oxamidide complex [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf(NCO)]$_4$ ([**1**-(**NCO**)]$_4$) in 51% yield (eq 1). The benzene-d_6 ^{13}C NMR spectrum of the ^{13}C-labeled isotopologue exhibits a singlet centered at 163.2 ppm, consistent with oxamidide formation and a symmetric [$N_2C_2O_2$]$^{4-}$ core of the molecule. The solid-state (KBr) infrared stretching frequency of the oxamidides was located at 1570 cm^{-1}. The tetrametallic hafnocene oxamidide is a new structural motif that is likely a consequence of the less sterically encumbered cyclopentadienyl rings that allow assembly of four hafnocene subunits.



Formation of the tetrametallic hafnocene oxamidide [**1**-(**NCO**)]$_4$ was also confirmed by single-crystal X-ray diffraction. A representation of the molecular structure is presented in Figure 1. While a definitive distinction of O and N atoms by X-ray diffraction is tenuous, the best fit of the data is the transoid disposition of the like atoms consistent with all zirconocene and hafnocene complexes prepared to date.[18,20] The C−C and N−C distances of 1.544(7) and 1.301(6)/1.260(6) Å are typical of the values previously observed with dimeric zirconocene and hafnocene oxamidides prepared from CO-induced N_2 bond cleavage.[18,20]

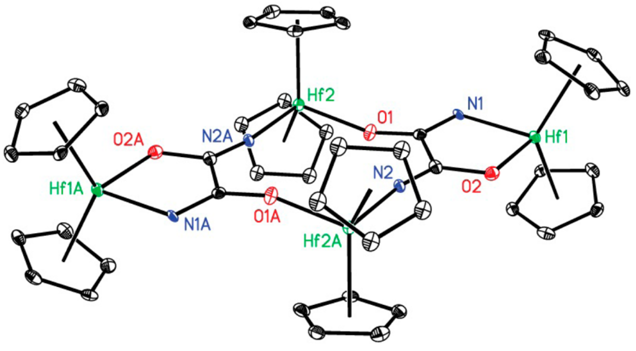
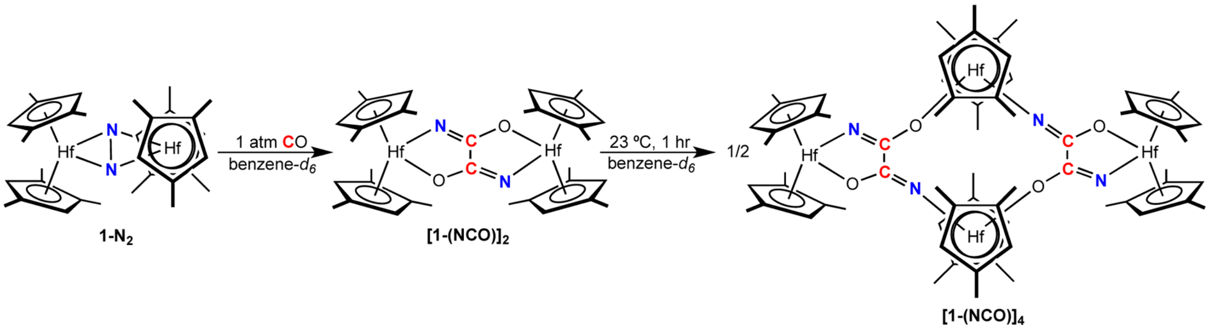


Figure 1. Representation of the solid-state structure of [**1**-(**NCO**)]$_4$ with 30% probability ellipsoids. Hydrogen atoms, cyclopentadienyl methyl groups, and one molecule of tetrahydrofuran are omitted for clarity. Half of the molecule has been generated by the symmetry operator −*x*, −*y*, −*z*.

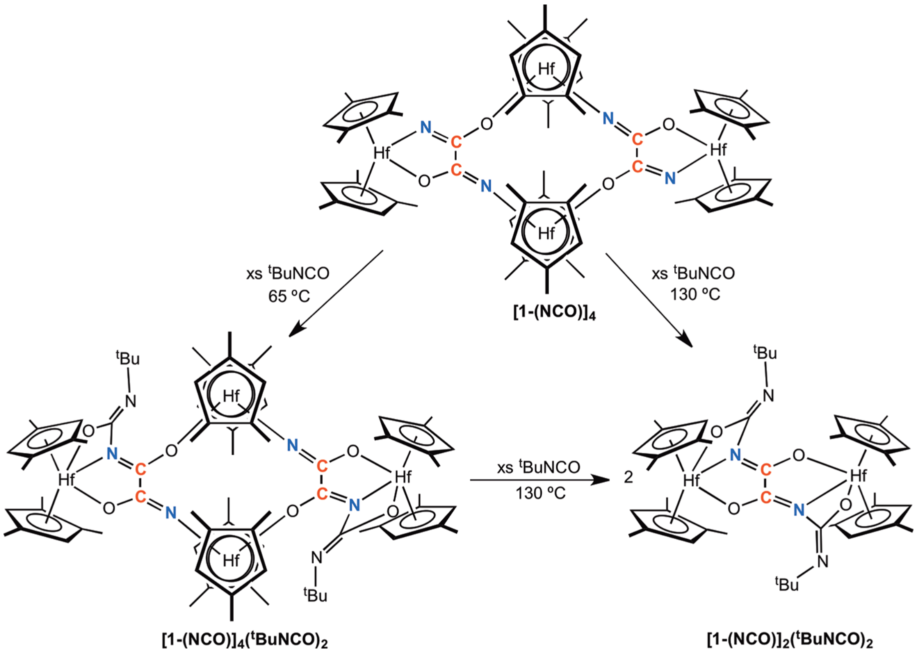
The observation of a new tetrametallic structural motif arising from dinitrogen carbonylation raised the question as to whether the more commonly observed dimeric hafnocene oxamidide is synthetically accessible and if it is an intermediate in the formation of [**1**-(**NCO**)]$_4$. Performing the carbonylation of **1-N$_2$** with 1 atm of CO at 23 °C and monitoring the progress of the reaction by NMR spectroscopy in benzene-d_6 allowed identification of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$($N_2C_2O_2$) ([**1**-(**NCO**)]$_2$). The ^{13}C, ^{15}N isotopologue [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$($^{15}N_2{}^{13}C_2O_2$) was prepared from ^{13}CO and $^{15}N_2$ gas and exhibited a triplet in the ^{13}C NMR spectrum centered at 158.9 ppm with $^1J_{CN}$ and $^2J_{CN}$ couplings of 3.9 Hz, consistent with N−C bond formation and similar to values for other oxamidide complexes of this type.[18,20] Accordingly, the benzene-d_6 ^{15}N NMR spectrum exhibited a triplet ($^1J_{C-N}$ = $^2J_{C-N}$ = 3.9 Hz) also confirming formation of N−C and C−C bonds from CO and N_2. The solid-state (KBr) infrared spectrum of [**1**-(**NCO**)]$_2$ exhibits a band at 1625 cm^{-1}, distinct from the band at 1570 cm^{-1} for [**1**-(**NCO**)]$_4$, allowing clear identification of the bimetallic and tetrametallic oxamidides. Notably, allowing red benzene-d_6 solutions of [**1**-(**NCO**)]$_2$ to stand for approximately 1 h at 23 °C (with or without a CO atmosphere) resulted in precipitation of a yellow solid identified as [**1**-(**NCO**)]$_4$, demonstrating the intermediacy of the dimeric compound (Scheme 2).

Reactivity of [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf(NCO)]$_4$. The reactivity of [**1**-(**NCO**)]$_4$ was explored with the goal of elaborating the oxamidide core and comparing it with the established chemistry of analogous dimeric hafnocene oxamidides.[18,21] We were particularly interested in exploring the

Scheme 2. Synthesis of [1-(NCO)]$_2$ and Its Conversion to [1-(NCO)]$_4$



Scheme 3. Cycloaddition of Excess ^{t}BuNCO to [1-(NCO)]$_4$ at 65 and 130 °C



number of hafnium−nitrogen bonds that are available for subsequent functionalization chemistry. Previous studies have demonstrated that the cycloaddition of heterocumulenes to dimeric hafnocene oxamidides is an effective strategy for elaboration of both of the Hf−N bonds of the $[N_2C_2O_2]^{4-}$ ligand.[21] Heating a THF solution of [**1-(NCO)**]$_4$ to 65 °C in the presence of excess (>4 equiv) ^{t}BuNCO for 18 h followed by recrystallization from toluene furnished yellow blocks identified as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4(^tBuNCO)_2$ ([**1-(NCO)**]$_4$(**^{t}BuNCO**)$_2$) in 55% yield. The C_{2h} symmetric product is a result of the [C═O] cycloaddition of the heterocumulene to two transoid disposed Hf−N bonds (Scheme 3).

Performing the cycloaddition reaction at 130 °C also resulted in additional N−C bond formation but instead yielded the bimetallic hafnocene $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(N_2C_2O_2)(^tBuNCO)_2$ ([**1-(NCO)**]$_2$(**^{t}BuNCO**)$_2$), where each Hf−N bond has been functionalized. Presumably cycloaddition across all four hafnium−nitrogen bonds disrupts the tetrametallic core to produce dimeric hafnocene complexes. To further probe this possibility, [**1-(NCO)**]$_4$(**^{t}BuNCO**)$_2$ was heated with excess ^{t}BuNCO over the course of 18 h at 130 °C. Complete conversion to **1-(NCO)**]$_2$(**^{t}BuNCO**)$_2$ was established by NMR spectroscopy. Both [**1-(NCO)**]$_4$(**^{t}BuNCO**)$_2$ and [**1-(NCO)**]$_2$(**^{t}BuNCO**)$_2$ were also characterized by X-ray diffraction, and representations of the molecular structures are given in Figures 2 and 3, respectively.

The 1,2-addition of primary silanes has also proven to be an effective means of functionalizing hafnocene oxamidide cores.[21] To evaluate whether all four Hf−N bonds could be functionalized in this manner and to explore the molecularity of the resulting complex, the reactivity of [**1-(NCO)**]$_4$ with primary silanes was studied. Addition of 4 equiv of $CySiH_3$ to a THF solution of [**1-(NCO)**]$_4$ at 23 °C for 2 h followed by recrystallization from a fluorobenzene−pentane mixture furnished colorless crystals identified as [**1-(NCO)**]$_2$(**CySiH$_3$**)$_2$ in 70% yield (eq 2). The identity of the product was established by X-ray diffraction (Figure 4), and the structure was of sufficient quality that the hydrogen atoms, including the hafnium hydrides, were located and refined. Performing the reaction with only 1 or 2 equiv of the silane produced a mixture of products containing [**1-(NCO)**]$_4$ and [**1-(NCO)**]$_2$(**CySiH$_3$**)$_2$.

Thermolysis of Hafnocene Oxamidides for the Synthesis of Cyanide Complexes. The thermal stability of the tetrametallic hafnocene oxamidide was also assayed. Heating a benzene solution of [**1-NCO**]$_4$ to 110 °C for 2 days followed by cooling to room temperature deposited colorless crystals of

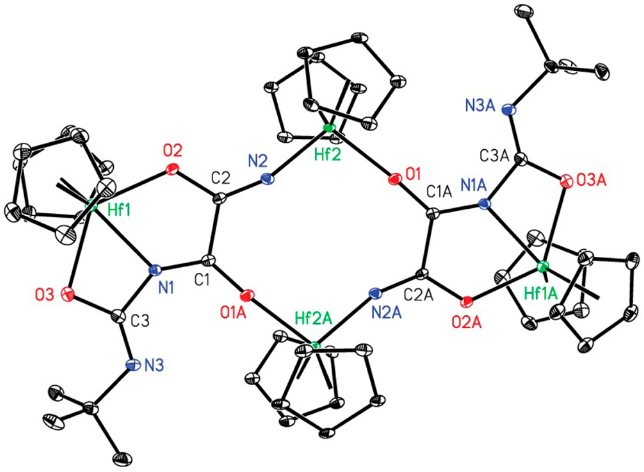


Figure 2. Representation of the solid-state structure of **[1-(NCO)]$_4$(^{t}BuNCO)$_2$** with 30% probability ellipsoids. One molecule of toluene, hydrogen atoms, and cyclopentadienyl methyl groups are omitted for clarity. Half of the molecule has been generated by the symmetry operator −*x*, −*y*, −*z*.

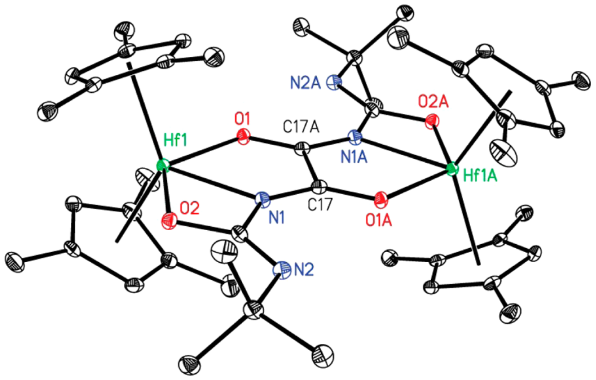
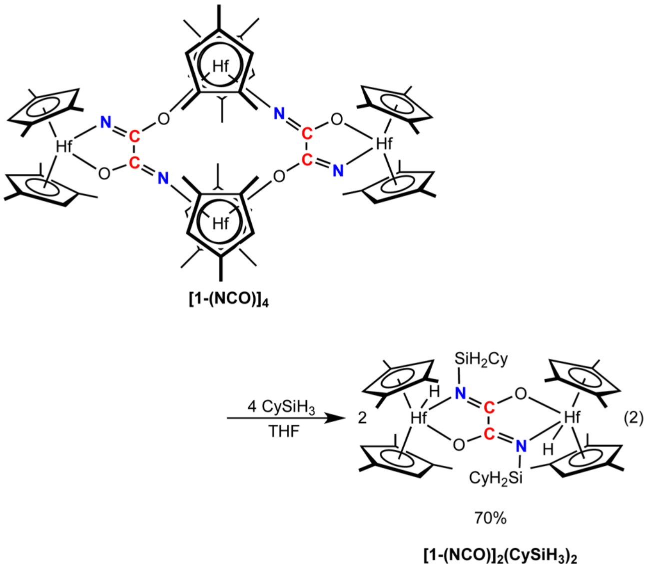


Figure 3. Representation of the solid-state structure of **[1-(NCO)]$_2$(^{t}BuNCO)$_2$** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.



[1-(NCO)]$_4$

[1-(NCO)]$_2$(CySiH$_3$)$_2$

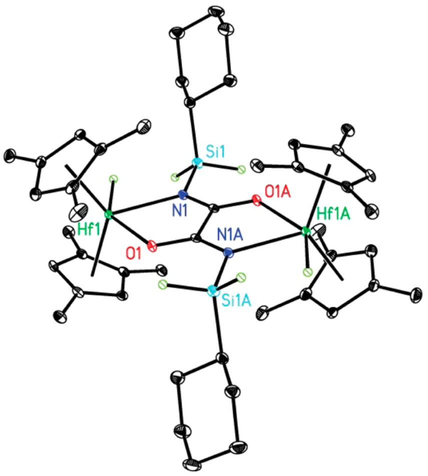
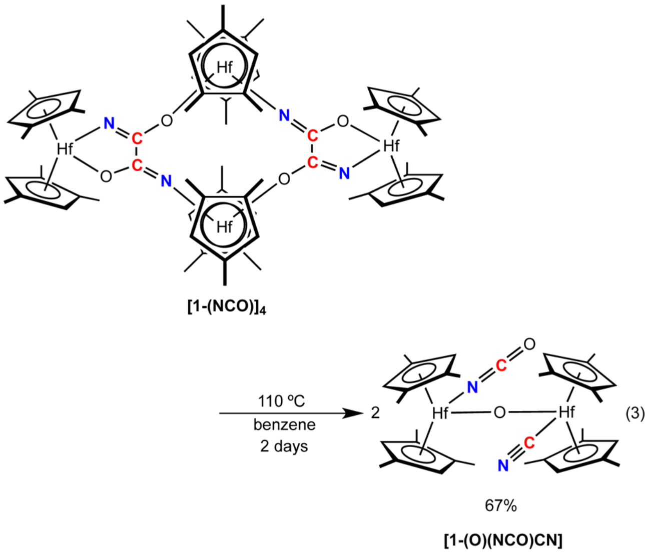


Figure 4. Representation of the solid-state structure of **[1-(NCO)]$_2$(CySiH$_3$)$_2$** with 30% probability ellipsoids. Hydrogen atoms, except those attached to Hf and Si, are omitted for clarity. Half of the molecule has been generated by the symmetry operator −*x*, −*y*, −*z*.

the μ-oxo dihafnocene isocyanate cyanide complex $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)](\mu\text{-}O)[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(CN)]$ (**[1-(O)(NCO)CN]**), arising from partial deoxygenation and isomerization of the oxamidide ligand (eq 3).



[1-(NCO)]$_4$

[1-(O)(NCO)CN]

The molecular structure of **[1-(O)(NCO)CN]** was confirmed by single-crystal X-ray diffraction (Figure 5) and is to our knowledge the first example of a structurally characterized hafnocene cyanide complex. Thewalt and co-workers have reported the synthesis and solid-state structures of $[(\eta^5\text{-}C_5H_5)_2Ti(CN)]_4$,[31] $[(\eta^5\text{-}C_5H_5)_2Ti(CN)(OMe)]$, and $[(\eta^5\text{-}C_5H_5)_2Ti(CN)]_2(O)$.[32] In the context of N_2 functionalization, Cummins and co-workers have reported the synthesis of a terminal molybdenum cyanide from the corresponding N_2-derived metal nitride compound[33] and have also used the same platform to develop a synthetic cycle for the synthesis of free organic nitriles.[34] In the structure of **[1-(O)(NCO)CN]**, typical bent metallocene coordination geometries are observed with Hf(1)−C(34) and C(34)−N(2) distances of 2.236(9) and 1.166(12) Å, respectively, for the terminal cyanide ligand. In solid-state structures of this type, the isocyanate and cyanide fragments are disordered over both metal centers. The ligands were modeled over both positions and refined freely.

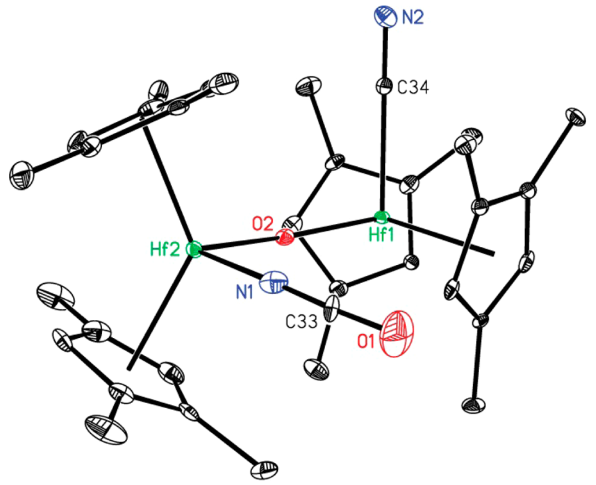


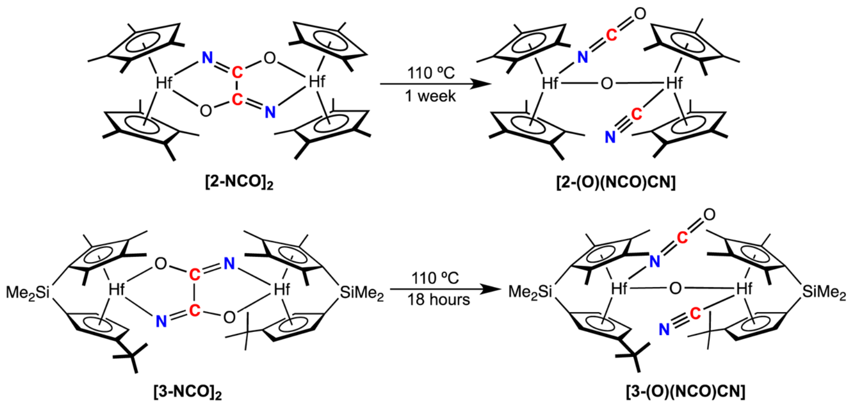
Figure 5. Representation of the solid-state structure of [**1**-(**O**)-(**NCO**)**CN**] with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The partial deoxygenation and isomerization of the oxamidide ligand in [**1-NCO**]$_4$ was also confirmed by multinuclear NMR spectroscopy. The benzene-d_6 ^{13}C NMR spectrum of [**1**-(**O**)(^{15}**N**^{13}**CO**)^{13}**C**^{15}**N**] exhibits a doublet centered at 135.4 ppm ($^1J_{C-N}$ = 32.8 Hz), diagnostic for a terminal hafnocene isocyanate, and a second doublet centered at 164.1 ppm ($^1J_{C-N}$ = 8.3 Hz), assigned to the cyanide ligand. Accordingly, the ^{15}N NMR spectrum exhibits two doublets at 94.15 and 324.15 ppm for the [NCO] and [CN] ligands, respectively. The benzene solution infrared spectrum of [**1**-(**O**)(**NCO**)**CN**] exhibits strong bands at 2223 and 2203 cm^{-1} for the isocyanate and cyanide ligands, respectively. These peaks shift appropriately to 2148 and 2138 cm^{-1} for [**1**-(**O**)(^{15}**N**^{13}**CO**)^{13}**C**^{15}**N**]. The spectroscopic data for [**1**-(**O**)-(**NCO**)**CN**] are identical with those previously reported for the hafnocene bis(isocyanate) complex [(η^5-C_5H_2-1,2,4-Me_3)$_2$Hf]$_2$(NCO)(μ_2-NCO),[25] establishing the correct identity of the compound as the isomeric μ-oxo dihafnium isocyanate cyanide. Thus, carbonylation of the pyridine-stabilized dihafnium nitride complexes provides a more facile entry point to [**1**-(**O**)(**NCO**)**CN**].

The possibility that the dimeric and tetrametallic oxamidide complexes are in equilibrium was explored. A recrystallized sample of pure [**1**-(**NCO**)]$_4$ was dissolved in benzene-d_6 and monitored by ^{1}H NMR spectroscopy. Over the course of 24 h at 23 °C, [**1**-(**NCO**)]$_4$ slowly converted to [**1**-(**O**)(**NCO**)**CN**] with no evidence for the formation of [**1-NCO**]$_2$ or any other intermediates. While direct observation of interconversion of both constituents of the equilibrium was not achieved by NMR spectroscopy, the reactivity of [**1-NCO**]$_4$ toward silanes and *tert*-butyl isocyanate suggests that such an equilibrium is likely operative.

The observation of oxamidide isomerization and partial deoxygenation upon thermolysis of [**1-NCO**]$_4$ raised the question of the generality of the transformation. Heating a benzene-d_6 solution of [(η^5-C_5Me_4H)$_2$Hf]$_2$($N_2C_2O_2$) ([**2-NCO**]$_2$) to 110 °C for 1 week resulted in clean formation of a new C_1-symmetric hafnocene product identified as the μ-oxo dihafnocene isocyanato cyanide complex [(η^5-C_5Me_4H)$_2$Hf-(NCO)](μ-O)[(η^5-C_5Me_4H)$_2$Hf(CN)] ([**2**-(**O**)(**NCO**)**CN**]; Scheme 4). Similar chemistry was observed with the C_2-symmetric isomer of the *ansa*-hafnocene oxamidide complex [Me_2Si(η^5-C_5Me_4)(η^5-C_5H_3-3-^{t}Bu)Hf]$_2$($N_2C_2O_2$) ([**3-NCO**]$_2$-C_2). Clean conversion to the isomerized product [Me_2Si(η^5-C_5Me_4)(η^5-C_5H_3-3-^{t}Bu)Hf(NCO)](μ-O)[Me_2Si(η^5-C_5Me_4)-(η^5-C_5H_3-3-^{t}Bu)Hf(CN)] ([**3**-(**O**)(**NCO**)**CN**]) was observed upon heating to 110 °C for 18 h in benzene. Both [**2**-(**O**)(**NCO**)**CN**] and [**3**-(**O**)(**NCO**)**CN**] were characterized by X-ray diffraction, and representations of the molecular structures are reported in Figures 6 and 7, respectively. [**3**-(**O**)(**NCO**)**CN**] contained a crystallographically imposed center of symmetry, with only half of the dimer being present in the asymmetric unit. Consequently, the cyanide and isocyanate ligands were disordered over the same metal center. The disorder was treated through the use of a PART command, which allowed both fragments to freely and separately refine. Additionally, because of the proximity of the two ligands and their similar electron densities, the final refinement was completed using the EADP command, giving each ligand atom similar anisotropic displacement parameters. The related compound [**2**-(**O**)(**NCO**)**CN**] was not generated by symmetry but displayed a similar disorder of the isocyanate and cyanide ligands. However, attempting to treat the disorder similarly through the use of PART commands was unsuccessful, and the final crystallographic model therefore displays larger than usual anisotropic displacement parameters for the disordered ligands. The ^{13}C NMR spectra of both compounds exhibit diagnostic peaks centered at 162.7 and 164.4 ppm for the terminal cyanide ligands. The ^{13}C NMR spectra of both compounds exhibit diagnostic peaks centered at 162.7 and 164.4 ppm for the terminal cyanide ligands.

Scheme 4. Thermal Isomerization of Hafnocene Oxamidide Complexes



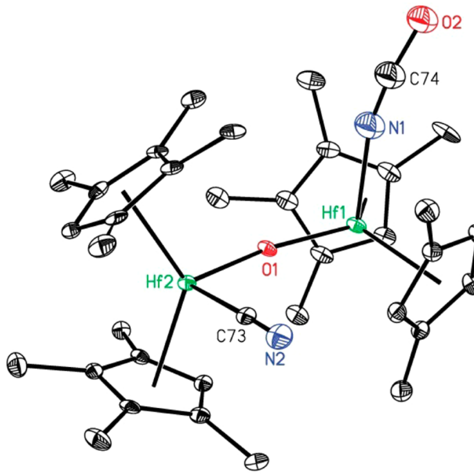


Figure 6. Representation of the solid-state structure of [**2**-(**O**)(**NCO**)**CN**] with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Only one of the two crystallographic independent molecules is shown. The isocyanate and cyanide ligands are disordered over two positions (see text).

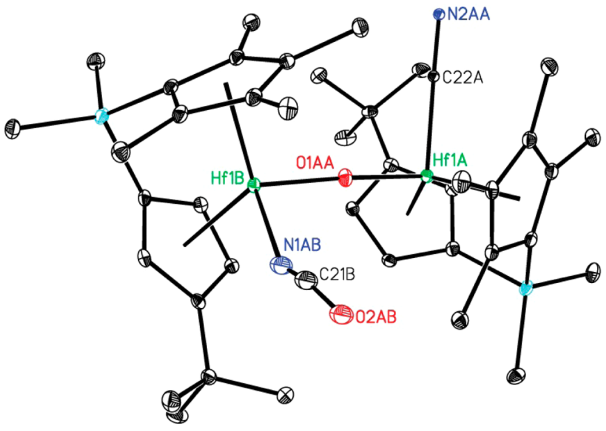
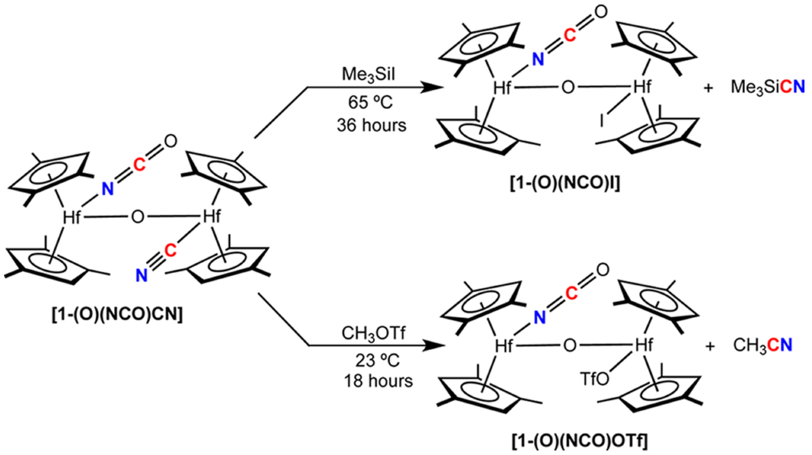


Figure 7. Representation of the solid-state structure of (*S*,*S*)-[**3**-(**O**)(**NCO**)**CN**] with 30% probability ellipsoids. Solvent, hydrogen atoms, and disordered cyanide/isocyanate groups are omitted for clarity. Half of the dimer has been generated by symmetry (see text).

Comparing the relative rates of partial deoxygenation−isomerization among the various metallocenes reveals no apparent trend as a function of molecularity. The *ansa*-hafnocene oxamidide [**3**-(**NCO**)]$_2$ undergoes the fastest rearrangement in the series (18 h at 110 °C), while the time scale for the tetrametallic compound [**1**-(**NCO**)]$_4$ is longer but comparable (48 h at 110 °C). Introduction of a methyl substituent on each cyclopentadienyl ring furnishes a dimeric hafnocene oxamidide compound that exhibits markedly improved stability toward isomerization, as complete conversion with [**2**-**NCO**]$_2$ requires thermolysis at 110 °C for 1 week. The origin of this effect is not understood at the present time.

The formation of a terminal cyanide ligand from thermal isomerization of hafnocene oxamidide complexes prompted examination of the reactivity of these compounds. We were particularly interested in determining whether the terminal isocyananate or cyanide is more labile and which more readily undergoes group transfer processes. Treatment of a benzene-d_6 solution of [**1**-(**O**)(**NCO**)**CN**] with Me_3SiI followed by heating to 65 °C for 3 days furnished a new C_2-symmetric hafnocene complex, identified as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(I)](\mu\text{-}O)[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]$ ([**1**-(**O**)(**NCO**)**I**]) and isolated in 81% yield (Scheme 5). Analysis of the volatiles from the reaction mixture by NMR spectroscopy allowed identification of Me_3SiCN as the byproduct of the reaction, confirming preferential group transfer of the terminal cyanide ligand. The benzene-d_6 ^{13}C NMR spectrum of [**1**-(**O**)(**N**^{13}**CO**)**I**] exhibited a diagnostic terminal isocyanate resonance at 135.5 ppm, and the solid-state infrared (KBr) displayed a strong band centered at 2221 cm^{-1} for the [NCO] ligand, which shifts appropriately to 2161 cm^{-1} upon ^{13}C labeling. The identity of the organometallic compound was also confirmed by single-crystal X-ray diffraction (Figure 8). The unit cell contained two crystallographically independent molecules with nearly identical structural parameters. For each of these molecules, the iodide ligand was disordered over both metal centers. The halide fragments were refined to 80/20 occupancy, and the isocyanate fragment was treated in a similar manner. The benzene-d_6 ^1H NMR spectrum of $Me_3Si^{13}CN$ (Figure 9), prepared from [**1**-(**O**)(**N**^{13}**CO**)^{13}**CN**] and Me_3SiI, exhibits a doublet centered at −0.22 ppm with a $^3J_{C-H}$ coupling of 2.7 Hz. The ^{13}C NMR spectrum of the same material exhibits a doublet at −2.1 ppm ($^2J_{C-C}$ = 5.0 Hz) for the [Me_3Si] group and an intense resonance at 126.9 ppm for the isotopically labeled nitrile carbon.

Scheme 5. Treatment of [1-(O)(NCO)CN] with Electrophiles and Synthesis of Me_3SiCN and CH_3CN from CO and N_2



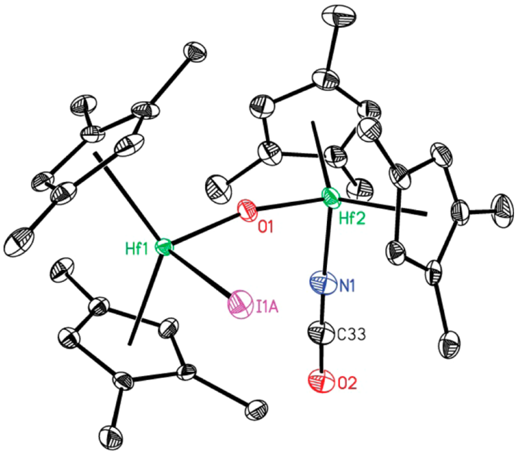


Figure 8. Solid-state structure of [**1-(O)(NCO)I**] with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. One of the two crystallographically independent molecules is shown; one disordered iodine atom is omitted for clarity.

Performing a similar experiment with CH_3OTf at 23 °C and [**1-(O)(NCO)CN**] also furnished $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(OTf)](\mu\text{-}O)[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]$ ([**1-(O)-(NCO)OTf**]) as a white solid in 91% yield (Scheme 5). As with the related iodo product, [**1-(O)(NCO)OTf**] exhibits a diagnostic ^{13}C NMR resonance at 135.9 ppm for the terminal isocyanate ligand and a strong band at 2221 cm^{-1} in the benzene-d_6 solution infrared spectrum. Analysis of the volatile reaction products by ^1H NMR spectroscopy following treatment of [**1-(O)(N^{13}CO)^{13}CN**] with CH_3OTf confirmed formation of $CH_3{}^{13}CN$, as evidenced by a doublet ($^2J_{C-H}$ = 9.9 Hz) centered at 0.57 ppm (Figure 9). Accordingly, one doublet ($^1J_{C-C}$ = 57.9 Hz) was observed at 0.40 ppm and an intense singlet was observed at 116.3 ppm in the ^{13}C NMR spectrum for the methyl and ^{13}C-labeled cyano groups, respectively.

■ CONCLUDING REMARKS

Carbonylation of the hafnocene dinitrogen complex $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$ with 4 atm of CO resulted in formation of a tetrametallic hafnocene oxamidide complex, a new structural motif arising from carbon monoxide induced N_2 cleavage. The more common dimeric hafnocene oxamidide $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(N_2C_2O_2)$ was observed by NMR spectroscopy when the carbonylation reaction was performed at slightly lower carbon monoxide pressure. The dimeric compound converts to the tetrametallic species over time in benzene-d_6 solution. Treatment of the tetrametallic hafnocene oxamidide with ^{t}BuNCO resulted in functionalization of two of the four Hf–N bonds via [C═O] cycloaddition. In contrast, addition of $CySiH_3$ resulted in 1,2-addition to all four hafnium–nitrogen bonds and furnished a dimeric hafnocene product. Thermolysis of the tetrametallic or previously reported dimeric hafnocene oxamidides resulted in partial deoxygenation and isomerization to μ-oxo dihafnocene complexes with terminal isocyanate and cyanide ligands. For the $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]$ derivative, addition of electrophiles such as Me_3SiI and CH_3OTf resulted in preferential group transfer of the cyano ligand, establishing a method to prepare organonitriles, albeit stoichiometrically, from CO and N_2.

■ EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard high-vacuum-line, Schlenk, or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[35] Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Carbon monoxide gas was passed through a column containing 4 Å molecular sieves before use. The hafnocene dinitrogen compound $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\mu_2,\eta^2{:}\eta^2\text{-}N_2)$[27] and the hafnocene oxami-

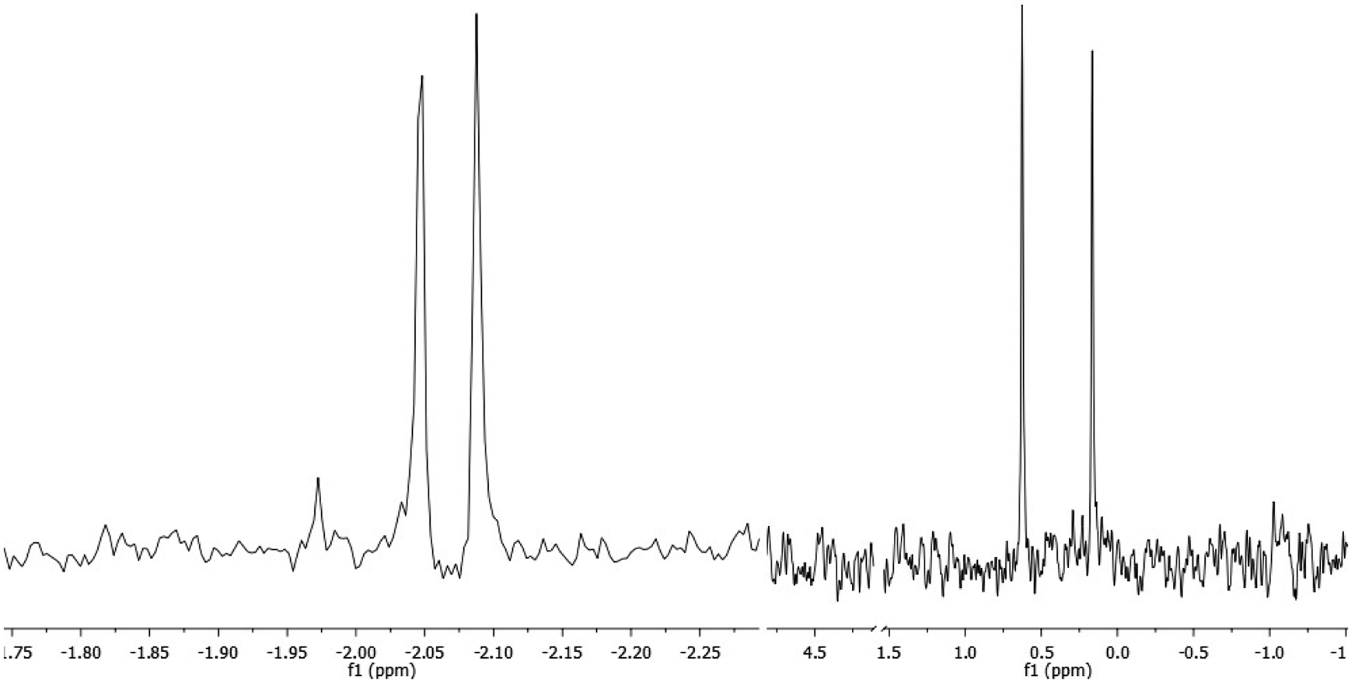


Figure 9. Benzene-d_6 ^1H NMR spectra of $Me_3Si^{13}CN$ (left) and $CH_3{}^{13}CN$ (right) at 23 °C.

dide complexes $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(N_2C_2O_2)$[25] and $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(N_2C_2O_2)$[21] were prepared according to literature procedures.

^1H 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 ^1H (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. 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 = 0.710 73 and 1.541 84 Å respectively). Preliminary data revealed the crystal system. The collection routine was optimized 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 $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$ ($[1\text{-}(NCO)]_4$). A thick-walled glass vessel was charged with 0.100 g (0.123 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\eta^2,\eta^2\text{-}N_2)$ and 10 mL of THF. On a high-vacuum line, the contents of the vessel were frozen and evacuated. Carbon monoxide gas (1 atm at 77 K) was then added. The reaction mixture was thawed and shaken vigorously for approximately 1 min, and a color change to light red was observed. The vessel was degassed and brought into the glovebox, and the solution was concentrated to approximately 2 mL in vacuo. Storage at −35 °C for 18 h resulted in deposition of 55 mg (0.032 mmol, 51%) of analytically pure bright yellow crystals identified as $[(C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$. Anal. Calcd for $C_{68}H_{88}Hf_4N_4O_4$: C, 46.95; H, 5.10; N, 3.22. Found: C, 46.70; H, 5.18; N, 2.91. ^1H NMR (benzene-d_6, 23 °C): δ 2.11 (s, 12H, C_5H_2-1,2,4-Me_3), 2.12 (s, 12H, C_5H_2-1,2,4-Me_3), 2.14 (s, 12H, C_5H_2-1,2,4-Me_3), 2.31 (s, 12H, C_5H_2-1,2,4-Me_3), 2.38 (s, 12H, C_5H_2-1,2,4-Me_3), 2.49 (s, 12H, C_5H_2-1,2,4-Me_3), 5.75 (d, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.80 (d, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.88 (d, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.96 (d, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3). ^1H NMR (THF-d_8, 23 °C): δ 2.10 (s, 12H, C_5H_2-1,2,4-Me_3), 2.12 (s, 12H, C_5H_2-1,2,4-Me_3), 2.13 (s, 12H, C_5H_2-1,2,4-Me_3), 2.16 (s, 12H, C_5H_2-1,2,4-Me_3), 2.18 (s, 12H, C_5H_2-1,2,4-Me_3), 2.31 (s, 12H, C_5H_2-1,2,4-Me_3), 5.69 (d, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.81 (d overlapped, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.88 (d, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.91 (d, $^4J_{HH}$ = 2.2, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 13.7, 13.7, 14.3, 14.4, 15.1, 15.5 (C_5H_2-1,2,4-Me_3), 112.3, 114.0, 114.5, 114.6, 115.1, 118.6, 119.1, 120.8, 121.5, 122.4 (C_5H_2-1,2,4-Me_3), 163.2 ($C_2O_2N_2$). $^{13}C\{^1H\}$ NMR (THF-d_8, 23 °C): δ 13.5, 13.6, 14.3, 14.9, 15.6, 16.0 (C_5H_2-1,2,4-Me_3), 112.3, 114.0, 114.4, 114.7, 115.2, 118.5, 119.4, 120.8, 121.7, 122.5 (C_5H_2-1,2,4-Me_3), 163.2 ($C_2O_2N_2$). IR (KBr): 1570 cm^{-1} (C═N).

Spectroscopic Characterization of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(N_2C_2O_2)$. A J. Young NMR tube was charged with 0.015 g (0.018 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(\eta^2{:}\eta^2\text{-}N_2)$ and 0.5 g of benzene-d_6. The tube was removed from the glovebox, and 1 atm of CO gas was added at ambient temperature. The solution was thawed and shaken until a color change to light red was observed. The resulting mixture was immediately analyzed by multinuclear NMR and IR spectroscopy. ^1H NMR (benzene-d_6, 23 °C): δ 2.06 (s overlapped, 12H, C_5H_2-1,2,4-Me_3), 2.07 (s overlapped, 24H, C_5H_2-1,2,4-Me_3), 5.63 (d, $^4J_{HH}$ = 2.6, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.72 (d, $^4J_{HH}$ = 2.6, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 13.5, 13.6, 15.2 (C_5H_2-1,2,4-Me_3), 114.7, 115.0, 120.2, 122.7, 123.0 (C_5H_2-1,2,4-Me_3), 158.9 (t, $^1J_{CN}$, $^2J_{CN}$ = 3.9, $N_2C_2O_2$). $^{15}N\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 371.07 (t, $^1J_{CN}$, $^2J_{CN}$ = 3.9, $\mathit{N}_2C_2O_2$). IR (KBr): 1625 cm^{-1} (C═N).

Preparation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_4(N_2C_2O_2)_2(^tBuNCO)_2$. A thick-walled glass vessel was charged with a stirbar, 0.035 g (0.021 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$, and 5 mL of THF. To this solution was added 0.010 g (0.082 mmol) of ^tBuNCO via microsyringe. The vessel was removed from the box, and the solution was stirred for 18 h at 65 °C. The solvent was removed in vacuo and the yellow residue recrystallized from toluene at −35 °C to give yellow blocks identified as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_4(N_2C_2O_2)_2(^tBuNCO)_2$ in 55% yield (22 mg, 0.012 mmol). Anal. Calcd for $C_{78}H_{106}Hf_4N_6O_6$: C, 48.35; H, 5.51; N, 4.34. Found: C, 48.59; H, 5.78; N, 3.98. ^1H NMR (benzene-d_6, 23 °C): δ 1.78 (s, 18H, $NC\mathit{Me}_3$), 2.07 (s, 12H, C_5H_2-1,2,4-Me_3), 2.09 (s, 12H, C_5H_2-1,2,4-Me_3), 2.21 (s, 12H, C_5H_2-1,2,4-Me_3), 2.26 (s, 12H, C_5H_2-1,2,4-Me_3), 2.30 (s, 12H, C_5H_2-1,2,4-Me_3), 2.34 (s, 12H, C_5H_2-1,2,4-Me_3), 5.71 (d, $^4J_{HH}$ = 2.4, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.79 (d, $^4J_{HH}$ = 2.4, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.93 (d, $^4J_{HH}$ = 2.4, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 6.24 (d, $^4J_{HH}$ = 2.4, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 13.5, 13.5, 13.9, 14.7, 15.3, 16.7 (C_5H_2-1,2,4-Me_3), 32.2 ($NC\mathit{Me}_3$), 53.1 ($NCMe_3$), 111.5, 111.5, 112.1, 114.3, 117.4, 118.6, 118.8, 120.0, 122.4, 122.6 (C_5H_2-1,2,4-Me_3), 160.5 (^tBuNCO), 161.0 (d, $^1J_{CC}$ = 77.6, $N_2C_2O_2$), 162.3 (d, $^1J_{CC}$ = 77.6, $N_2C_2O_2$). IR (C_6H_6): 1637, 1597 cm^{-1} (C═N).

Preparation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(N_2C_2O_2)(^tBuNCO)_2$. A thick-walled glass vessel was charged with a stirbar, 0.070 g (0.042 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$, and 5 mL of benzene. Via microsyringe, 0.019 g (0.160 mmol) of ^tBuNCO was added, the vessel was removed from the box, and the solution was stirred for 18 h at 130 °C. Slowly cooling the solution to room temperature deposited colorless crystals that were washed with pentane to furnish $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf]_2(N_2C_2O_2)(tBuNCO)_2$ in 45% yield (40 mg, 0.038 mmol). Anal. Calcd for $C_{44}H_{62}N_4O_4Hf_2$: C, 49.48; H, 5.85; N, 5.25. Found: C, 49.73; H, 5.96; N, 5.14. ^1H NMR (benzene-d_6, 23 °C): δ 1.66 (s, 18H, $OCNC\mathit{Me}_3$), 1.85 (s, 12H, C_5H_2-1,2,4-Me_3), 1.97 (s, 12H, C_5H_2-1,2,4-Me_3), 2.14 (s, 12H, C_5H_2-1,2,4-Me_3), 5.41 (d, 4H, $^4J_{HH}$ = 2.2, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.52 (d, 4H, $^4J_{HH}$ = 2.2, $C_5\mathit{H}_2$-1,2,4-Me_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 12.8, 12.9, 14.8 (C_5H_2-1,2,4-Me_3), 31.7 ($OCNC\mathit{Me}_3$), 52.0 ($OCNCMe_3$), 115.2, 115.3, 116.7, 121.4, 122.8 (C_5H_2-1,2,4-Me_3), 147.9 ($OCNCMe_3$), 160.8 (t, $^1J_{CN}$, $^2J_{CN}$ = 13.4, $N_2C_2O_2$). $^{15}N\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 191.82 (t, $^1J_{CN}$, $^2J_{CN}$ = 13.4, $\mathit{N}_2C_2O_2$). IR (C_6H_6): 1651, 1562 cm^{-1} (C═N).

Preparation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(H)](N_2C_2O_2)(SiH_2Cy)_2$. A scintillation vial was charged with a stirbar, 0.035 g (0.021 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$, and 5 mL of THF. To this solution was added 0.010 g (0.082 mmol) of cyclohexylsilane via microsyringe, and the contents of the vial were stirred at room temperature for 2 h. The solvent and volatiles were removed in vacuo, and the colorless residue was recrystallized from fluorobenzene−pentane to give colorless crystals identified as $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(H)]_2(N_2C_2O_2)(SiH_2Cy)_2$ in 70% yield (33 mg, 0.029 mmol). Anal. Calcd for $C_{46}H_{72}N_2O_2Si_2Hf_2$: C, 50.31; H, 6.61; N, 2.55. Found: C, 50.53; H, 6.70; N, 2.27. ^1H NMR (benzene-d_6, 23 °C): δ 1.05−1.68 (m overlapped, 10H, cyclohexyl $C\mathit{H}_2$), 1.78 (s, 12H, C_5H_2-1,2,4-Me_3), 1.85 (m, 5H, cyclohexyl $C\mathit{H}_2$), 2.14 (s, 12H, C_5H_2-1,2,4-Me_3), 2.21 (m, 7H, cyclohexyl $C\mathit{H}_2$), 2.26 (s, 12H, C_5H_2-1,2,4-Me_3), 4.94 (s, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 5.10 (s, 4H, $Si\mathit{H}_2Cy$), 5.62 (s, 4H, $C_5\mathit{H}_2$-1,2,4-Me_3), 9.37 (s, 2H, Hf-H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 23 °C): δ 13.1 (C_5H_2-1,2,4-Me_3), 13.6 (C_5H_2-1,2,4-Me_3), 16.3 (C_5H_2-1,2,4-Me_3), 24.9 (cyclohexyl CH), 26.1, 27.6, 28.6, 29.5 (cyclohexyl CH_2), 109.0, 109.3, 114.2, 114.8, 120.2 (C_5H_2-1,2,4-Me_3), 174.6 ($N_2C_2O_2$). IR (C_6D_6): 1581 (C═N), 2082, 2112, 2160 cm^{-1} (Si-H).

Preparation of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(CN)](\mu\text{-}O)[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]$. *Method 1.* A J. Young NMR tube was charged with 0.059 g (0.034 mmol) of $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)]_4$ and 1 mL of benzene. The suspension was heated for 2 days at 110 °C. Upon slow cooling of the solution to room temperature, $[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(NCO)](\mu\text{-}O)[(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf(CN)]$ crystallized from the reaction mixture as colorless needles suitable for X-ray diffraction. The supernatant was removed, and the remaining crystals were washed with pentane to afford 0.037 g (0.043 mmol, 63%) of white crystals identified as [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(NCO)](μ-O)[(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(CN)].

Method 2. A thick-walled glass vessel was charged with a stirbar, 0.049 g (0.060 mmol) of [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf]$_2$(η^2:η^2-N$_2$), and 0.007 g (0.064 mmol) of 4-methoxypyridine. Toluene (10 mL) was added, and a color change to blue-green was observed. On a high-vacuum line, the contents of the vessel were frozen, the vessel was evacuated, and CO gas (1 atm at 77 K) was admitted. The vessel was warmed to room temperature and shaken vigorously for 1 min, whereupon a color change to light red was observed. The solution was stirred at room temperature for 18 h, over which time a color change to dark brown was observed. The solvent was removed in vacuo, and the brown oil was washed with 10 mL of cold pentane and dried in vacuo to furnish 0.040 g (0.046 mmol, 77%) of an analytically pure white powder. Anal. Calcd for C$_{34}$H$_{44}$Hf$_2$N$_2$O$_2$: C, 46.95; H, 5.10; N, 3.22. Found: C, 46.76; H, 4.84; N, 3.13. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.72 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 1.92 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.14 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.16 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.18 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.52 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 5.06 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.24 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.72 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.99 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 13.0, 13.8, 14.9, 15.2, 15.2, 15.4 (C$_5$H$_2$-1,2,4-*Me*$_3$), 112.8, 113.3, 114.9, 115.3, 117.6, 118.9, 118.9, 119.4, 124.6, 126.0 (*C*$_5$H$_2$-1,2,4-Me$_3$), 134.6 (Hf-NCO), 164.2 (Hf-CN). ^{1}H NMR (dichloromethane-d_2, 23 °C): δ 1.92 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 1.99 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.16 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.33 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.38 (s overlapped, 12H, C$_5$H$_2$-1,2,4-*Me*$_3$), 5.56 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.68 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.70 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.85 (d, 2H, $^4J_{\text{HH}}$ = 2.2, C$_5$*H*$_2$-1,2,4-Me$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 12.9, 13.6, 13.6, 15.2, 15.3, 15.4 (C$_5$H$_2$-1,2,4-*Me*$_3$), 112.7, 113.2, 115.5, 115.6, 117.3, 118.4, 119.0, 119.4, 124.2, 126.0 (*C*$_5$H$_2$-1,2,4-Me$_3$), 135.4 (d, $^1J_{\text{CN}}$ = 32.8, NCO), 164.1 (d, $^1J_{\text{CN}}$ = 8.3, CN). ^{15}N{^{1}H} NMR (benzene-d_6, 23 °C): δ 94.15 (d, $^1J_{\text{CN}}$ = 32.8, *N*CO), 324.15 (d, $^1J_{\text{CN}}$ = 8.3, CN). IR (benzene-d_6): 2223 (NCO), 2203 (CN), 2163 (^{13}CN), 2148 (^{15}N^{13}CO), 2138 cm^{-1} (^{13}C^{15}N).

Preparation of [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(NCO)](μ-O)[(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(I)]. A J. Young NMR tube was charged with 12 mg (0.014 mmol) of [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(CN)](μ-O)[(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(NCO)], 2.1 μL (0.015 mmol) of iodotrimethylsilane, and 0.5 mL of benzene. The solution was warmed to 65 °C for 36 h before the volatiles were removed in vacuo and the residue was washed with 2 × 5 mL of cold pentane to furnish 46 mg (0.045 mmol, 81%) of an analytically pure white solid identified as [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(I)](μ-O)[(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(NCO)]. The reported yield is from four combined NMR tubes. Crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated fluorobenzene solution at −35 °C for 4 days. Scale-up of this reaction was hampered by the relative insolubility of [**1-(O)(CN)(NCO)**] in benzene. Due to this complication, the stoichiometry of the reaction was more difficult to control on larger scales and resulted in the formation of unwanted side products. Pure product was obtained most reliably on an NMR scale. Anal. Calcd for C$_{33}$H$_{44}$Hf$_2$INO$_2$: C, 40.84; H, 4.57; N, 1.44. Found: C, 40.67; H, 4.66; N, 1.66. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.73 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 1.91 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.18 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.20 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.22 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.45 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 5.27 (d, 2H, $^4J_{\text{HH}}$ = 1.9, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.30 (d, 2H, $^4J_{\text{HH}}$ = 1.9, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.91 (d, 2H, $^4J_{\text{HH}}$ = 1.9, C$_5$*H*$_2$-1,2,4-Me$_3$), 6.24 (d, 2H, $^4J_{\text{HH}}$ = 1.9, C$_5$*H*$_2$-1,2,4-Me$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 13.0, 13.9, 15.1, 15.4, 16.0, 16.5 (C$_5$H$_2$-1,2,4-*Me*$_3$), 114.0, 114.2, 114.5, 114.6, 117.5, 119.0, 119.4, 120.1, 124.1, 126.3 (*C*$_5$H$_2$-1,2,4-Me$_3$), 135.5 (Hf-NCO). IR (C$_6$D$_6$): 2221 cm^{-1} (NCO), 2161 cm^{-1}(N^{13}CO). Data for free Me$_3$SiCN are as follows. ^{1}H NMR (benzene-d_6, 23 °C): δ −0.22 (d, 9H, $^3J_{\text{CH}}$ = 2.7, *Me*$_3$SiCN). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ −2.1 (d, $^2J_{\text{CC}}$ = 5.0, *Me*$_3$SiCN), 126.9 (Me$_3$Si*C*N). IR (C$_6$D$_6$): 2190 cm^{-1} (CN), 2140 cm^{-1} (^{13}CN).

Preparation of [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(OTf)](μ-O)[(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(NCO)]. A 20 mL scintillation vial was charged with 36 mg (0.041 mmol) of [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(NCO)](μ-O)[(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(CN)], 5.00 μL (0.046 mmol) of methane trifluoromethylsulfonate, and 0.5 mL of toluene. The solution was stirred for 18 h at 23 °C, after which time the volatiles were removed in vacuo and the residue was washed with cold diethyl ether to afford an analytically pure white solid identified as [(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(OTf)](μ-O)[(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf(NCO)] in 90% (0.037 mmol, 37 mg) yield. Anal. Calcd for C$_{34}$H$_{44}$F$_3$Hf$_2$NO$_5$S: C, 41.13; H, 4.47; N, 1.41. Found: C, 41.01. H, 4.97; N, 1.54. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.74 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 1.94 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.05 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.12 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.16 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 2.17 (s, 6H, C$_5$H$_2$-1,2,4-*Me*$_3$), 5.24 (d, 2H, $^4J_{\text{HH}}$ = 2.5, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.78 (d, 2H, $^4J_{\text{HH}}$ = 2.5, C$_5$*H*$_2$-1,2,4-Me$_3$), 5.87 (d, 2H, $^4J_{\text{HH}}$ = 2.5, C$_5$*H*$_2$-1,2,4-Me$_3$), 6.15 (d, 2H, $^4J_{\text{HH}}$ = 2.5, C$_5$*H*$_2$-1,2,4-Me$_3$). ^{19}F NMR (benzene-d_6): −76.1 (C*F*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 13.0, 13.2, 13.3, 13.8, 14.9, 15.3 (C$_5$H$_2$-1,2,4-*Me*$_3$), 113.8, 114.6, 116.7, 117.1, 118.5, 119.7, 120.1, 122.9, 123.4, 126.5 (*C*$_5$H$_2$-1,2,4-Me$_3$), 135.9 (Hf-NCO). IR (C$_6$D$_6$): 2221 (NCO), 2161 cm^{-1} (N^{13}CO). Data for free MeCN are as follows. ^{1}H NMR (benzene-d_6, 23 °C): δ 0.57 (d, 3H, $^2J_{\text{CH}}$ = 9.9, C*H*$_3$CN). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 0.40 (d, $^1J_{\text{CC}}$ = 57.9, *C*H$_3$CN), 116.3 (CH$_3$*C*N).

Preparation of [(η^5-C$_5$Me$_4$H)$_2$Hf(NCO)](μ-O)[(η^5-C$_5$Me$_4$H)$_2$Hf(CN)]. A J. Young NMR tube was charged with 0.100 g (0.107 mmol) of [(η^5-C$_5$Me$_4$H)$_2$Hf]$_2$(N$_2$C$_2$O$_2$) and 1 mL of benzene. The suspension was heated at 110 °C for 8 days before the volatiles were removed in vacuo, and [(η^5-C$_5$Me$_4$H)$_2$Hf(NCO)](μ-O)[(η^5-C$_5$Me$_4$H)$_2$Hf(CN)] was recrystallized from the crude reaction mixture as colorless blocks by the slow evaporation of a toluene solution at 23 °C. The supernatant was removed, and the remaining crystals were washed with pentane to furnish 0.054 g (0.058 mmol, 54%) of a light yellow solid identified as [(η^5-C$_5$Me$_4$H)$_2$Hf(CN)](μ-O)[(η^5-C$_5$Me$_4$H)$_2$Hf(NCO)]. Anal. Calcd for C$_{38}$H$_{52}$Hf$_2$N$_2$O$_2$: C, 49.30; H, 5.66; N, 3.03. Found: C, 49.02; H, 5.48; N, 2.77. ^{1}H NMR (benzene-d_6, 23 °C): δ 1.60 (s, 3H, C$_5$*Me*$_4$H), 1.68 (s, 3H, C$_5$*Me*$_4$H), 1.78 (s, 3H, C$_5$*Me*$_4$H), 1.82 (s, 3H, C$_5$*Me*$_4$H), 1.91 (s, 3H, C$_5$*Me*$_4$H), 1.95 (s, 3H, C$_5$*Me*$_4$H), 1.96 (s, 3H, C$_5$*Me*$_4$H), 1.97 (s, 3H, C$_5$*Me*$_4$H), 2.00 (s, 6H, C$_5$*Me*$_4$H), 2.10 (s, 3H, C$_5$*Me*$_4$H), 2.16 (s, 3H, C$_5$*Me*$_4$H), 2.23 (s, 3H, C$_5$*Me*$_4$H), 2.46 (s, 3H C$_5$*Me*$_4$H), 2.52 (s, 3H, C$_5$*Me*$_4$H), 2.71 (s, 3H, C$_5$*Me*$_4$H), 5.21 (s, 1H, C$_5$Me$_4$*H*), 5.33 (s, 1H, C$_5$Me$_4$*H*), 5.54 (s, 1H, C$_5$Me$_4$*H*), 6.07 (s, 1H, C$_5$Me$_4$*H*). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ 11.43, 11.73, 11.82, 12.21, 12.29, 12.69, 12.86, 12.93, 13.23, 13.28, 13.36, 13.48, 13.52, 13.61, 13.73, 13.80 (C$_5$*Me*$_4$H), 112.5, 113.9, 114.8, 115.2, 115.3, 115.4, 115.5, 115.6, 116.6, 118.5, 121.0, 121.5, 122.1, 122.5, 122.8, 122.9, 123.2, 124.9, 125.7, 125.8 (*C*$_5$Me$_4$H), 135.6 (Hf-NCO), 164.4 (Hf-CN). IR (KBr): 2223 cm^{-1} (NCO).

Preparation of ([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Hf(NCO))(μ-O)([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Hf(CN)). A thick-walled glass vessel was charged with 0.160 g (0.162 mmol) of ([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Hf)$_2$(μ_2-N$_2$) and 10 mL of toluene. The vessel containing the dark purple solution was removed from the glovebox and degassed on a high-vacuum line, and 1 atm of CO gas was admitted at 77 K. The resulting dark red solution was stirred for 2 h before the CO was removed in vacuo and replaced with 1 atm of N$_2$ gas. The dark red solution was then heated to 110 °C with rapid stirring for 18 h. The volatiles were removed from the resulting brown solution in vacuo, and the oily brown residue was recrystallized from a minimum amount of diethyl ether at −35 °C to afford 0.075 g (0.072 mmol, 47% yield) of an analytically pure white solid identified as ([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-tBu)]Hf(CN))(μ-O)([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Hf(NCO)) from multiple batches. Colorless crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated THF solution stored at −35 °C for 3 days. Anal. Calcd for C$_{42}$H$_{60}$Hf$_2$N$_2$O$_2$Si$_2$: C, 48.59; H, 5.83; N, 2.70. Found: C, 48.51; H, 5.87; N, 2.41. ^{1}H NMR (benzene-d_6, 23 °C): δ 0.42 (s, 3H, Si*Me*$_3$), 0.49 (s, 3H, Si*Me*$_3$), 0.58 (s, 3H, Si*Me*$_3$), 0.59 (s, 3H, Si*Me*$_3$), 1.39 (s, 9H, C$_5$H$_3$C*Me*$_3$), 1.61 (s, 9H, C$_5$H$_3$C*Me*$_3$), 1.79 (s, 3H, C$_5$*Me*$_4$), 1.86 (s, 3H, C$_5$*Me*$_4$), 1.90 (s, 3H, C$_5$*Me*$_4$), 1.95 (s, 3H, C$_5$*Me*$_4$), 2.02 (s, 3H, C$_5$*Me*$_4$), 2.13 (s, 3H, C$_5$*Me*$_4$), 2.20 (s, 3H, C$_5$*Me*$_4$), 2.39 (s, 3H, C$_5$*Me*$_4$), 5.27 (m, 1H, C$_5$*H*$_3$CMe$_3$), 5.42 (m, 1H, C$_5$*H*$_3$CMe$_3$), 5.89 (m, 1H, C$_5$*H*$_3$CMe$_3$), 6.05 (m, 1H, C$_5$*H*$_3$CMe$_3$), 6.46 (m, 1H, $\mathrm{C_5}H_3\mathrm{CMe_3}$), 6.49 (m, 1H, $\mathrm{C_5}H_3\mathrm{CMe_3}$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C): δ −0.5, −0.4, 0.1, 0.2 (Si*Me*$_2$), 11.8, 12.1, 13.8, 14.1, 14.4, 14.9, 15.0, 15.6 ($\mathrm{C_5}Me_4$), 31.3, 31.8 ($\mathrm{C_5H_3C}Me_3$), 33.8, 33.9 ($\mathrm{C_5H_3}C\mathrm{Me_3}$), 100.0, 101.4, 106.4, 106.9, 108.0, 108.3, 108.4, 110.4, 112.4, 112.6, 118.5, 118.6, 121.9, 122.3, 126.0, 129.7, 132.9, 133.3, 154.0, 155.0 (Cp C), 135.8 (NCO), 162.7 (CN). IR (C_6H_6): 2228 cm^{-1} (NCO).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic details for [**1-(NCO)**]$_4$, [**1-(NCO)**]$_4$(**^{t}BuNCO**)$_2$, [**1-(NCO)**]$_2$(**^{t}BuNCO**)$_2$, [**1-(NCO)**]$_2$(**CySiH$_3$**)$_2$, [**1-(O)(NCO)CN**], [**2-(O)(NCO)CN**], (*S*,*S*)-[**3-(O)(NCO)CN**], and [**1-(O)(NCO)I**] and figures giving representative NMR spectra and a representation of the solid-state structure of (***R***,***R***)-[**3-(O)(NCO)CN**]. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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