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Functionalization of Hafnium Oxamidide Complexes Prepared from CO-Induced N_2 Cleavage

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Abstract: Functionalization of the nitrogen atoms in the hafnocene oxamidide complexes $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(N_2C_2O_2)$ and $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(N_2C_2O_2)$, prepared from CO-induced N_2 bond cleavage, was explored by cycloaddition and by formal 1,2-addition chemistry. The *ansa*-hafnocene variant, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(N_2C_2O_2)$, undergoes facile cycloaddition with heterocumulenes such as ^{t}BuNCO and CO_2 to form new N−C and Hf−O bonds. Both products were crystallographically characterized, and the latter reaction demonstrates that an organic ligand can be synthesized from three abundant and often inert small molecules: N_2, CO, and CO_2. Treatment of $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(N_2C_2O_2)$ with I_2 yielded the monomeric iodohafnocene isocyanate, $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf(I)(NCO)$, demonstrating that C−C bond formation is reversible. Alkylation of the oxamidide ligand in $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(N_2C_2O_2)$ was explored due to the high symmetry of the complex. A host of sequential 1,2-addition reactions with various alkyl halides was discovered and both *N*- and *N*,*N*′-alkylated products were obtained. Treatment with Brønsted acids such as HCl or ethanol liberates the free oxamides, $H(R^1)NC(O)C(O)N(R^2)H$, which are useful precursors for *N*,*N*′-diamines, *N*-heterocyclic carbenes, and other heterocycles. Oxamidide functionalization in $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(N_2C_2O_2)$ was also accomplished with silanes and terminal alkynes, resulting in additional N−Si and N−H bond formation, respectively.

Introduction

Coupling the cleavage of the strong N≡N triple bond of atmospheric dinitrogen with nitrogen−carbon bond-forming reactions is an attractive synthetic route to nitrogen-containing organic molecules,[1−3] as the high energy and fossil fuels costs of the Haber−Bosch industrial ammonia synthesis would be avoided.[4−6] One approach to achieving this goal is to use a soluble transition metal complex to promote the N_2 cleavage reaction, followed by elaboration of the resulting metal nitrido species in subsequent steps with the appropriate reagents to effect N−C bond formation.[7−9] The three-coordinate molybdenum(III) compound, $Mo(N(^tBu)\text{-}3,5\text{-}Me_2\text{-}C_6H_3)_3$, has been a focal point of such studies, as this molecule is isolobal with a nitrogen atom and promotes N_2 cleavage at low temperature.[10−12] The resulting molybdenum nitride, $NMo(N(^tBu)\text{-}3,5\text{-}Me_2\text{-}C_6H_3)_3$, has served as a nitrogen source for organic molecules from treatment with trifluoroacetic anhydride[7] and has been incorporated into a cycle for the synthesis of organic nitriles.[8] Sita and co-workers have since reported a dinuclear tantalum end-on dinitrogen complex that promotes the cleavage of N_2 at low temperatures (<0 °C) and undergoes subsequent hydrosilylation to form a silylimido upon treatment with $PhSiH_3$.[13] Kawaguchi and co-workers have described the formation of a diniobium-bridging nitrido species following reductive elimination of H_2 from the corresponding tetrahydride species. Addition of CH_3I resulted in successive alkylation of the nitrogen atoms.[14]

An alternative strategy is ligand-induced N_2 bond cleavage where N≡N scission and N−C bond formation occur in a single transformation. This approach is potentially broader in scope, as the transition metal complex does not need to supply all six electrons for N_2 cleavage and a host of reagents to promote the desired chemistry are plausible. Sobota and Janas provided early experimental precedent for the viability of this route with the discovery of *N*,*N*-dimethylformamide formation following treatment of an ill-defined titanium dinitrogen complex with carbon monoxide and subsequently CH_3I.[15] More recently, Fryzuk and co-workers have reported a rich N_2 cleavage and functionalization chemistry to form tantalum imides and nitrides from

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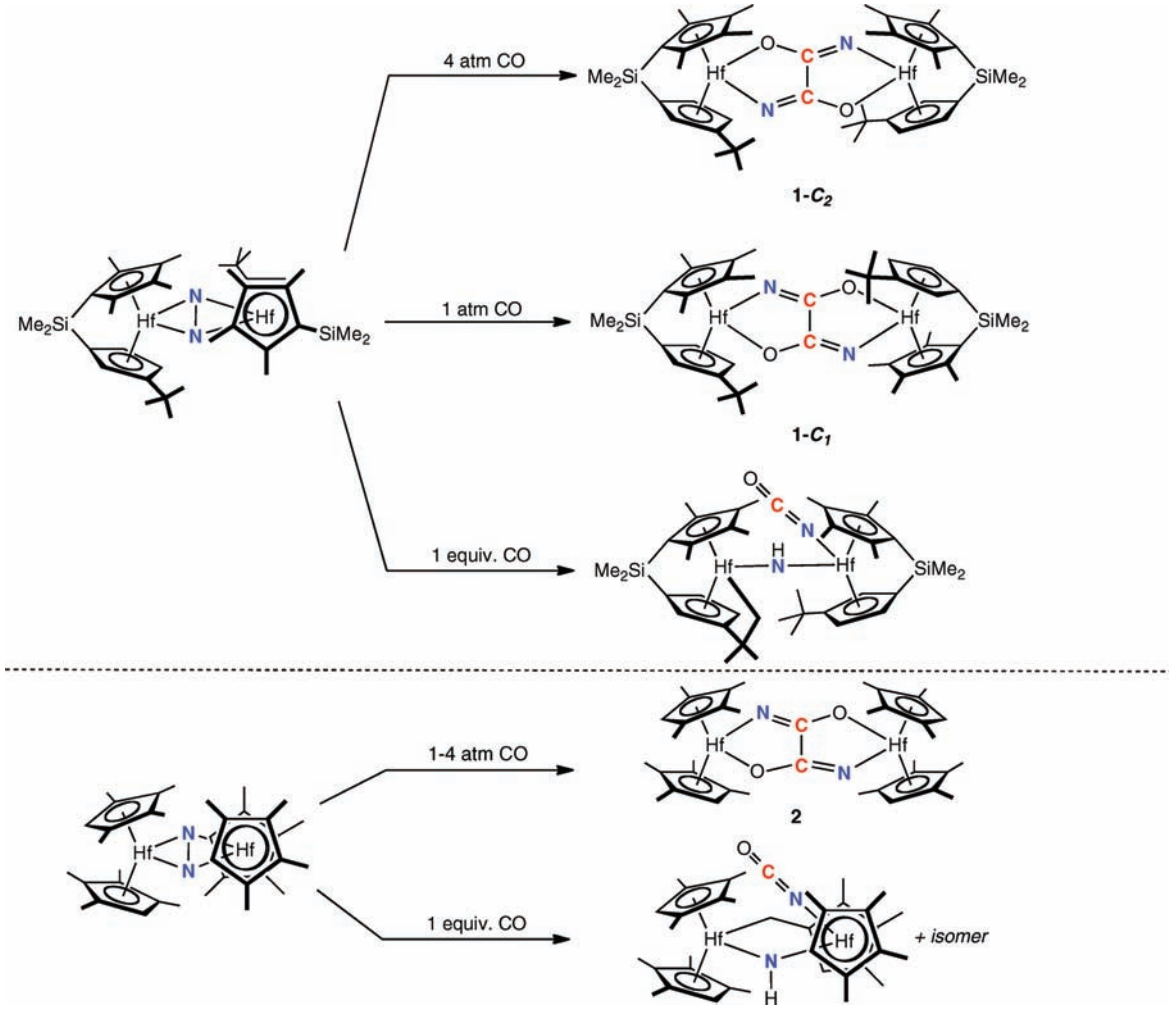
Scheme 1. CO-Induced N_2 Cleavage by Hafnocene Dinitrogen Complexes



addition of simple hydride reagents such as boranes,[16,17] silanes,[18,19] alanes,[20] and zirconium hydrides[21] to $([NPN]Ta)_2(\mu\text{-}H)_2(\mu_2,\eta^1,\eta^2\text{-}N_2)$ (NPN = $PhP(CH_2SiMe_2NPh)_2$).[22]

Zirconocene and hafnocene dinitrogen complexes with strongly activated, side-on-bound N_2 ligands offer rich functionalization chemistry,[23] including hydrogenation to ammonia[24−26] and N−C bond formation via isocyanate[27] and CO_2 insertion[28,29] as well as stepwise addition of electrophiles such as CH_3OTf to form metal-bound diazenide and hydrazonato compounds.[30] The *ansa*-hafnocene derivative, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Hf]_2(\mu_2, \eta^2, \eta^2\text{-}N_2)$, exhibits one of the most activated N−N bonds in this family of compounds, as evidenced by an elongated N−N distance of 1.457(5) Å.[31] Carbonylation with 1−4 atm of CO at 23 °C resulted in facile N−N bond cleavage, with concomitant formation of two N−C bonds and one new C−C bond (Scheme 1).[31] The resulting bridging, tetraanionic ligand, $[N_2C_2O_2]^{4-}$, was termed "oxamidide", as it is a conjugate base of oxamide, $H_2NC(O)C(O)NH_2$. Performing the carbonylation with only 1 equiv of carbon monoxide also resulted in CO-induced bond cleavage, forming terminal isocyanate and bridging imido ligands (Scheme 1). The latter likely result from C−H activation by a transient μ-nitrido dihafnium species. The generality of the carbonylation reaction was recently explored within a series of zirconocene and hafnocene complexes with side-on-bound N_2 ligands.[32] In all four cases examined, oxa-

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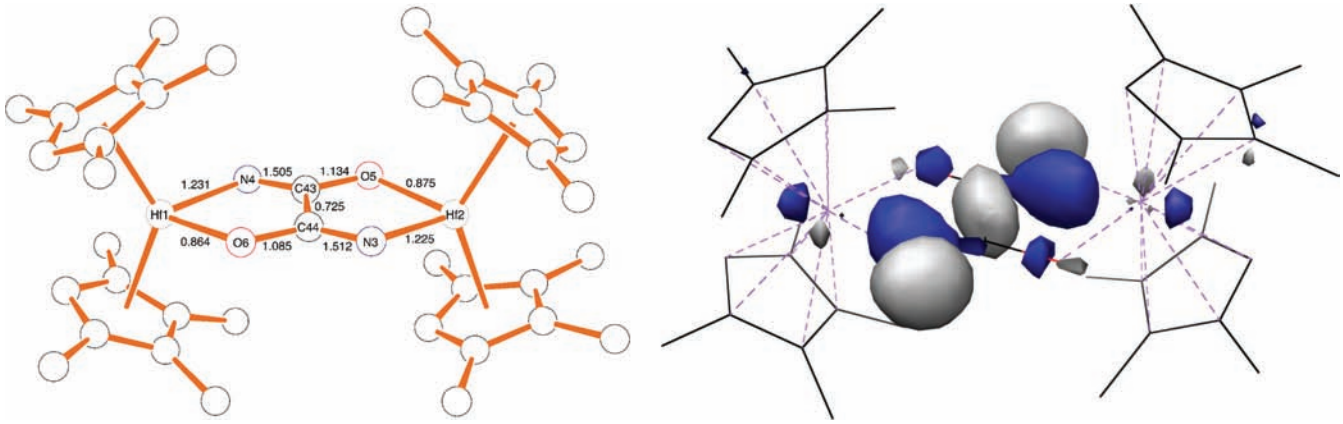


Figure 1. DFT-computed (B3LYP functional) Mayer bond orders and the highest occupied molecular orbital of **2**.

midide formation was observed. For the Zr congeners, dinitrogen activation is typically less pronounced, and zirconocene dicarbonyl complexes were also formed in small amounts, demonstrating that N_2 loss was competitive with CO-induced cleavage.

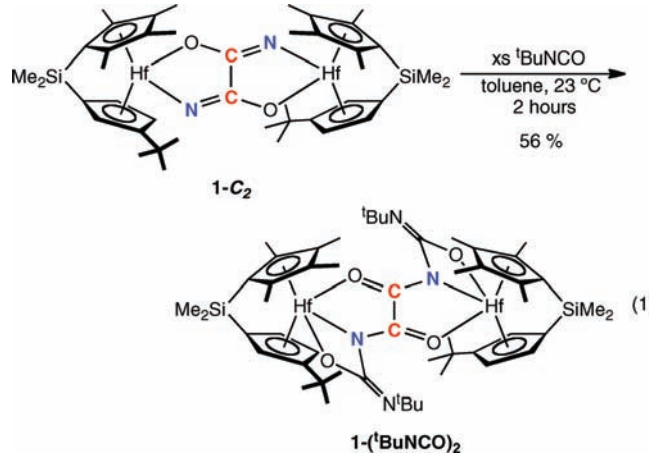
The oxamidide ligands formed from CO-induced N_2 bond cleavage present a unique opportunity to assemble N-containing organic molecules from atmospheric nitrogen. One encouraging feature of this approach is that the N≡N bond cleavage event, likely one of the most difficult transformations in the sequence, has been accomplished under mild conditions. The remaining challenges are to further elaborate the $[N_2C_2O_2]^{4-}$ core into value-added products and to release it from the metal. Here we describe additional N−C bond-forming reactions in hafnocene oxamidide complexes by cycloaddition of heterocumulenes and by 1,2-addition of various alkyl halides, silanes, and alkynyl C−H bonds. Facile cycloaddition of carbon dioxide was observed and demonstrates that organic ligands can be synthesized from three abundant and often inert small molecules: N_2, CO, and CO_2. In the cases of alkyl halide addition, subsequent treatment with Brønsted acids released free *N*-alkyl and *N*,*N*′-dialkyl oxamides, which are useful synthons for diamines, *N*-heterocyclic carbenes, and other heterocycles.

Results and Discussion

The electronic structure of the hafnocene oxamidide complexes was determined using full-molecule DFT calculations to provide guiding principles for subsequent reactivity studies. Due to its higher symmetry and relative simplicity, calculations were carried out with **2** using the B3LYP functional. Figure 1 presents the Mayer bond orders determined from the calculations as well as the HOMO of the molecule. The Hf−N bond order of 1.231 indicates multiple bond character, arising from π-donation of the oxamidide nitrogen, and suggests that cycloaddition reactivity[33−35] to elaborate the nitrogen may be possible. The HOMO of the molecule is composed principally of oxamidide nitrogen lone-pair character in the metallocene wedge, indicating that these atoms may be further elaborated by serving as nucleophiles or as bases.

Oxamidide Functionalization via Cycloaddition of Heterocumulenes. The possibility of cycloaddition-type reactivity with the metallocene oxamidides was explored by the addition of heterocumulenes. Only hafnocene oxamidide complexes **1** and **2** were studied, as the zirconium congeners suffer from chemistry derived from N_2 loss that is competitive with dinitrogen carbonylation.

Our laboratory previously reported that addition of isocyanates to $[(\eta^5\text{-}C_5Me_4H)Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ resulted in formation of nitrogen−carbon bonds arising from both insertion and cycloaddition reactions with the hafnium−nitrogen bonds in the dinitrogen complex with the heterocumulene.[27] Inspired by this result, similar reactivity was explored with the *ansa*-hafnocene oxamidide complex, **1**. As described previously,[31] this complex can be synthesized as either the C_1- or C_2-symmetric isomer, depending on the pressure of CO used for dinitrogen carbonylation and cleavage. Due to its relative ease of isolation, the C_2-symmetric isomer, **1-*C*$_2$** (as a racemic mixture), was used for these studies. Addition of an excess (∼5 equiv) of *tert*-butyl isocyanate to a toluene solution of **1-*C*$_2$**, followed by removal of the volatiles and recrystallization from diethyl ether at −35 °C, furnished a yellow solid identified as **1-(^{t}BuNCO)$_2$**, arising from double isocyanate cycloaddition to the oxamidide, in 56% yield (eq 1).



The benzene-d_6 ^{1}H and ^{13}C NMR spectra of **1-(^{t}BuNCO)$_2$** exhibit the number of peaks consistent with formation of a single, C_2-symmetric product. Complete peak assignments are

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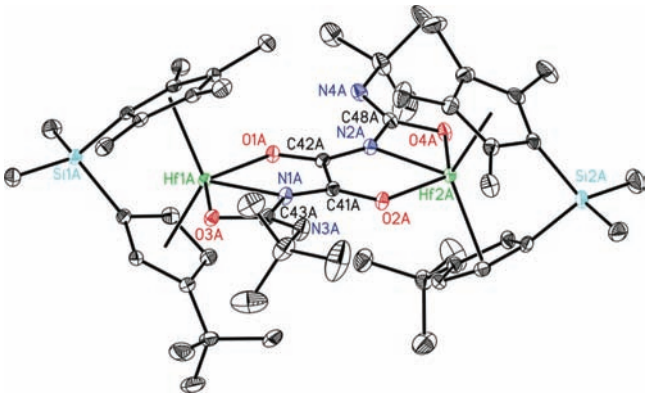


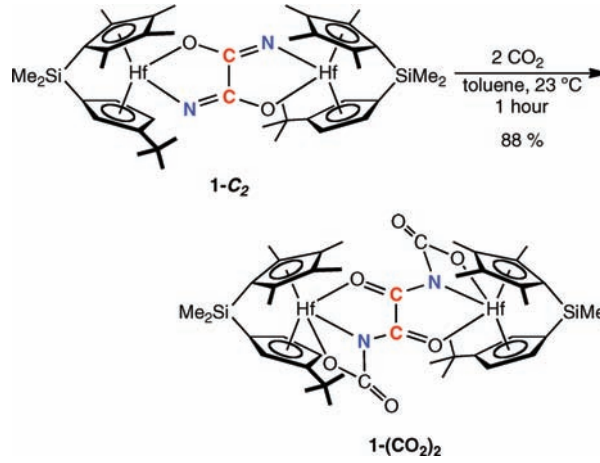
Figure 2. Representation of the solid-state structure of **(*S*,*S*)-1-(ᵗBuNCO)₂** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

reported in the Experimental Section. Diagnostic bands at 1673 and 1647 cm^{-1} were observed in the solid-state (KBr) infrared spectrum. The identity of the preferred diastereomer was established by X-ray diffraction. A representation of the (*S*,*S*) enantiomer of **1-(ᵗBuNCO)₂** is presented in Figure 2; the (*R*,*R*) enantiomer is reported in the Supporting Information. Selected bond distances and angles of all crystallographically characterized compounds in this work as well as those for the hafnocene oxamidides **1** and **2** are presented in Table 1. The crystallographic data are consistent with the solution NMR spectroscopic studies and establish formation of a C_2-symmetric product arising from cycloaddition of the C═O portion of the heterocumulene. Key features are the elongated C−N bonds and contracted C−O bonds in the oxamidate core in comparison to the parent oxamidide **1-*C*₂**, consistent with increased C−N single bond and C═O double bond character. The stereochemistry of the starting hafnocene is preserved in the cycloaddition product, placing the *tert*-butyl groups of the isocyanate groups *syn* to the *tert*-butyl substituents on the cyclopentadienyl ligand. The newly formed core maintains a nearly planar configuration, and the hafnocene subunits are slightly twisted with respect to each other with a dihedral angle of 1.7°.

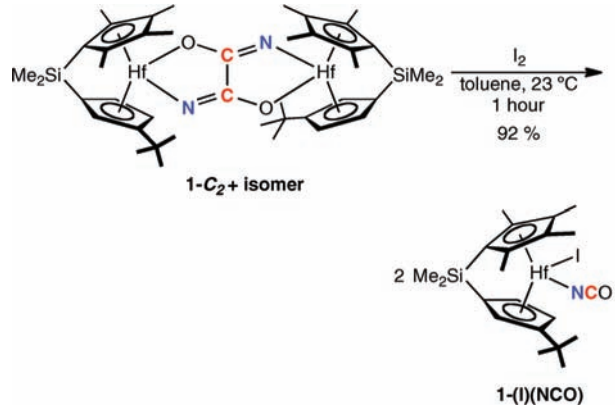
The clean and facile cycloaddition of ᵗBuNCO to **1-*C*₂** prompted exploration of related chemistry with carbon dioxide. Our laboratory has previously reported dinitrogen functionalization with CO_2 to yield, following treatment with an electrophile, various dicarboxylated hydrazines. For $[(\eta^5\text{-}C_5Me_4H)_2\text{-}Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$,[28] an 85:15 mixture of *N*,*N* and *N*,*N*′ insertion products was obtained, while for the *ansa*-zirconocene, $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, exclusive *N*,*N*′ insertion was observed.[29] In both compounds, only insertion, not cycloaddition, of the two CO_2 molecules into the metal−nitrogen bonds was observed.

Addition of 2 equiv of CO_2 gas to a frozen toluene solution of **1-*C*₂**, followed by warming to ambient temperature and stirring for 1 h, produced a yellow solution from which a yellow solid identified as **1-(CO₂)₂** was isolated in 88% yield (eq 2). The benzene-d_6 ^1H and ^{13}C NMR spectra exhibit the number of peaks consistent with formation of a single diastereomer of a C_2-symmetric product. Isotopic labeling with both ^{13}CO and $^{13}CO_2$ gases produced multiplets arising from an AA′XX′ spin system centered at 163.18 and 150.54 ppm with with $^2J_{C-C} = {}^3J_{C-C} = 1.5$ Hz,[36] confirming CO_2 incorporation (Figure 3, right). The solid-state structure was determined by X-ray diffraction, and a representation of the (*S*,*S*)-enantiomer is presented in Figure 3 (left). Similar to **1-(ᵗBuNCO)₂**, the crystallographic data establish cycloaddition of two molecules of CO_2 to each of the hafnium−nitrogen bonds with concomitant formation of new N−C and Hf−O bonds. The metrical parameters for **1-(CO₂)₂** demonstrate that in the solid state the compound exhibits C−N elongation and C═O contraction similar to that observed with **1-(ᵗBuNCO)₂**. The core is nearly planar and the dihedral angle between the hafnocene subunits is 3.0°.

The cycloaddition reactivity of the hafnocene oxamidide complex with carbon dioxide contrasts the CO_2 insertion chemistry observed from carbonylation of the hafnocene and zirconocene N_2 compounds. Perhaps most notably, the synthesis of **1-(CO₂)₂** demonstrates that an organic ligand can be synthesized from three typically inert and abundant small molecules: N_2, CO, and CO_2.



Oxidative C−C Cleavage of Hafnocene Oxamidides with Iodine. In addition to heterocumulenes, the reactivity of the *ansa*-hafnocene oxamidide **1** with iodine was also explored. Addition of 1 equiv of I_2 to a toluene solution of **1** (as a mixture of C_1 and C_2 isomers) yielded a single new C_1-symmetric product, identified as the monomeric iodo *ansa*-hafnocene isocyanate, **1-(I)(NCO)**, as a pale yellow solid (eq 3).



The presence of a terminal isocyanate ligand formed from oxidative C−C cleavage of the oxamidide core was established by a combination of IR spectroscopy, multinuclear NMR experiments, and X-ray diffraction. The solid-state infrared spectrum (KBr) exhibits a strong band centered at 2229 cm^{-1},

(36) Values reported as an average for the AA′XX′ spin system. See the Supporting Information for details.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **1**,[31] **2**,[32] and Compounds Crystallographically Characterized in This Work

	1-C_2	**1-(^{t}BuNCO)$_2$**	**1-$(CO_2)_2$**	**2**[c]	**2-$(PhSiH_3)_2$**[d]	**2-$(CH_3I)_2$**[d]
d(Hf−N)	2.062(2)	2.165(2)	2.174(2)	2.043(5) (E3)	2.322(4)	2.358(6)
	2.0557(19)	2.175(2)	2.186(2)	2.057(4) (E1)		
d(Hf−O)	2.0570(16)	2.2440(18)	2.2528(18)	2.058(5) (E4)	2.253(3)	2.211(4)
	2.0584(17)	2.2115(18)	2.2432(17)	2.062(4) (E2)		
d(C−C)	1.534(3)	1.506(4)	1.524(4)	1.531(8)	1.499(8)	1.468(9)
d(C−N)	1.270(3)	1.295(3)	1.299(3)	1.299(7) (E3)	1.317(5)	1.295(9)
	1.275(3)	1.302(3)	1.300(3)	1.320(8) (E1)		
d(C−O)	1.341(3)	1.267(3)	1.258(3)	1.303(7) (E4)	1.273(5)	1.277(9)
	1.339(3)	1.269(3)	1.259(3)	1.297(7) (E2)		
d(N−E)[a]		1.417(3)	1.420(3)		1.786(4)	1.47(1)
		1.407(3)	1.429(3)			
d(Hf−X)[b]		2.2054(18)	2.1880(18)		1.91(4)	2.9788(7)
		2.1970(19)	2.2081(19)			

[a] E denotes heteroatom in the newly formed bond to nitrogen (e.g., C, Si). [b] X denotes heteroatom in the newly formed bond to hafnium (e.g., I, H, O). [c] E1/E3 and E2/E4 are indistinguishable by crystallography. [d] Centrosymmetry relates both halves of the molecule.

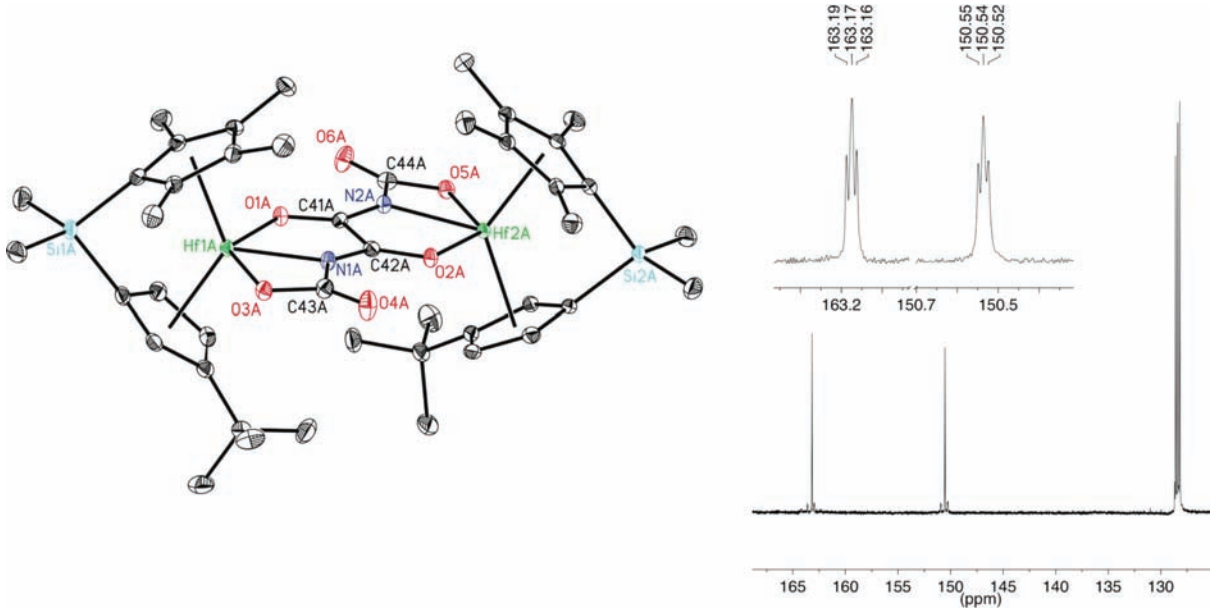


Figure 3. (Left) Molecular structure of **(*S*,*S*)-1-$(CO_2)_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. (Right) Benzene-d_6 ^{13}C NMR spectrum of **1-$^{13}C_2$-($^{13}CO_2$)$_2$** prepared from ^{13}CO and $^{13}CO_2$.

diagnostic of a hafnocene terminal isocyanate.[31] The ^{13}C NMR spectrum of **1-(I)($N^{13}CO$)** exhibits a broad peak centered at 136.81 ppm due to broadening from the quadrupolar ^{14}N nucleus (Figure 4, right). In the ^{15}N-labeled isotopologue, **1-(I)($^{15}N^{13}CO$)**, this peak splits into a well-resolved doublet ($^1J_{N-C}$ = 33.0 Hz), confirming the presence of an N−C bond assembled from N_2 and CO.

The identity of the observed diastereomer was confirmed by single-crystal X-ray diffraction. A representation of the solid-state structure is presented in Figure 4 (left) and confirms the formation of the terminal isocyanate *syn* to the *tert*-butyl ligand. Independent synthesis of **1-(I)(NCO)** was also achieved by stirring a THF slurry of $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}^tBu)HfI_2$ and AgNCO at 80 °C for 3 days. Analysis of the product by ^{1}H and ^{13}C NMR spectroscopy established formation of the same diastereomer as from C−C bond cleavage of the C_1 -and C_2-symmetric *ansa*-hafnocene oxamidides. The distances and angle for the terminal hafnocene isocyanate ligand are statistically indistinguishable from the corresponding values in the bimetallic hafnocene μ-imide isocyanate compound reported previously[31] and are also comparable to those of the recently reported hafnium isocyanate compounds.[32]

Preliminary investigations into the cycloaddition chemistry of the unlinked hafnocene oxamidide **2** with organic isocyanates and carbon dioxide as well as C−C cleavage chemistry with I_2 were also explored. Initial results and analysis by NMR spectroscopy indicated that the expected oxamidate and iodohafnium isocyanate products are formed, as in the case of the *ansa*-hafnocene. However, these compounds were formed in low yield and accompanied by considerable amounts of unidentified insoluble, intractable byproducts.

Functionalization Attempts with Terminal and Internal Alkynes. Alkynes have proven effective substrates for cycloadditions across early transition metal compounds with multiple bond character to nitrogen,[35,41d] For terminal alkynes, this approach has been extended to dinitrogen functionalization.[37,38] These results inspired the addition of terminal and internal alkynes to the hafnocene oxamidide complex **2**. Addition of a 10-fold excess of either diphenylacetylene or 2-butyne to **2** produced no reaction at ambient temperature and gradual

(37) Morello, L.; Love, J. B.; Patrick, B. O.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2004**, *126*, 9480.
(38) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 7901.

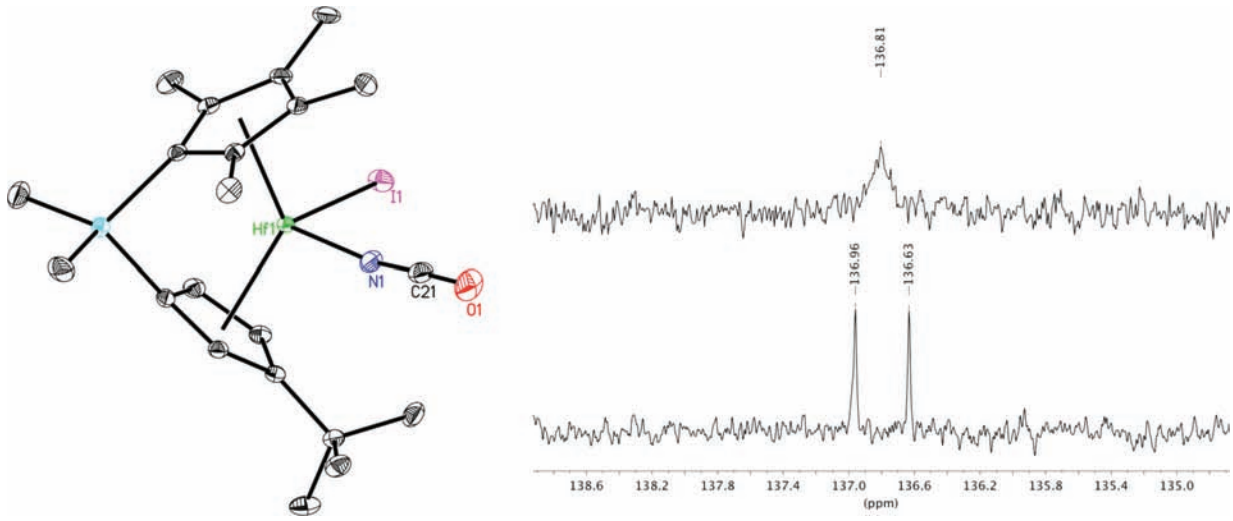
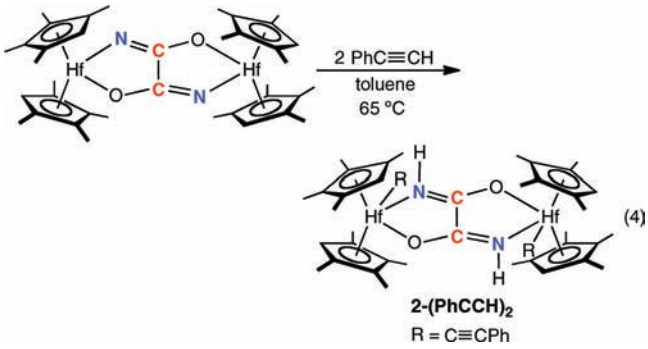


Figure 4. (Left) Molecular structure of **(*S*)-1-(I)(NCO)**. Hydrogen atoms are omitted for clarity. (Right) Isocyanate region of the ^{13}C NMR spectrum of **1-(I)(N^{13}CO)** (top) and **1-(I)(^{15}N^{13}CO)** (bottom) in benzene-d_6.

decomposition upon heating to 100 °C for 24 h. In light of these unsuccessful attempts at cycloaddition, terminal alkynes were targeted in hopes of accessing the products of carbon−hydrogen bond activation. The addition of a slight excess of phenylacetylene to **2** resulted in complete conversion, after 1 h at 65 °C, to the dimeric oxamidato hafnium acetylide product, **2-(PhCCH)$_2$** (eq 4).



(4)

Benzene-d_6 ^1H and ^{13}C NMR spectroscopic characterization established the C_{2h} symmetry of the complex and C−H activation of the acetylenic C−H bond. The concomitant formation of new N−H bonds was confirmed by the observed splitting of the N−H proton (^1H NMR) and the $N_2{}^{13}C_2O_2$ carbon (^{13}C NMR) in the AA′XX′ non-first-order spin system[39] upon isotopic labeling of the oxamidate core with ^{13}CO, as well as by multinuclear HSQC experiments. Infrared spectroscopy also supports the formation of N−H and acetylide functionalities, with stretching frequencies of 3371 and 2087 cm^{-1}, respectively.

Functionalization of Hafnocene Oxamidides with Alkyl Halides and Silanes. The cycloaddition reactivity and C−H bond activation chemistry observed with the hafnium−nitrogen bonds in **1** and heterocumulenes and with **2** and terminal alkynes prompted study into other classes of functionalization reactions. The 1,2-additions of carbon−hydrogen bonds,[33,40,41] dihydrogen,[42] and alkyl halides[33,34] are all well-established reactions for group 4 transition metal compounds with metal−nitrogen bonds.[43] Our attention focused on the alkylation and silylation of the hafnocene oxamidide complexes due to the utility of substituted oxamides as slow-release fertilizers and as synthons for various nitrogen-containing organic molecules such as diamines, *N*-heterocyclic carbenes, and *N*-heterocycles. The tetramethylated hafnocene oxamidide complex **2** was used for these studies due to its high symmetry and ease of synthesis compared to the isomers of **1**. Furthermore, the DFT results with **2** suggested nucleophilic and basic oxamidide nitrogens. The zirconocene oxamidide complexes reported previously were not studied due to N_2 loss chemistry that is competitive with dinitrogen carbonylation.[32]

Addition of 1 equiv of CH_3I to a toluene solution of **2** at 23 °C, followed by solvent removal and washing with cold pentane, furnished a yellow solid, identified as **2-(CH$_3$I)**, arising from a single 1,2-addition of the alkyl halide across a Hf−N bond (Scheme 2). Formation of a new nitrogen−carbon bond was confirmed by preparation of various combinations of ^{13}C and ^{15}N isotopologues from ^{13}CO, $^{13}CH_3I$, and $^{15}N_2$, for which ^{13}C and ^{15}N NMR spectra were obtained (N-*CH*$_3$, $^1J_{C-N}$ = 5.3 Hz, $^2J_{C-C}$ = 3.0 Hz, $^3J_{C-C}$ = 1.8 Hz; C−C, $^1J_{C-C}$ = 75.3 Hz). Representative spectra are presented in the Supporting Information (Figure S1). The benzene-d_6 ^1H NMR spectrum is also diagnostic. The C_{2h}-symmetric starting material, **2**, was cleanly and quantitatively converted to a C_s-symmetric molecule with inequivalent hafnocene subunits.

Other products of a single hafnocene oxamidide alkylation were also prepared. Addition of 1 equiv of ethyl iodide to a benzene-d_6 solution of **2** resulted in rapid 1,2-addition to form the N-ethylated product, **2-(CH$_3$CH$_2$I)**, in quantitative yield as judged by ^1H and ^{13}C NMR spectroscopy (eq 5). Similar results were obtained with $PhCH_2Br$. A single *N*-benzylation of **2** occurred over the course of 1 h at 23 °C in benzene-d_6 (eq 5).

(39) Coupling constants could not be determined because the simulated AA′XX′ spectrum generated infinite solutions that fit the experimental data.

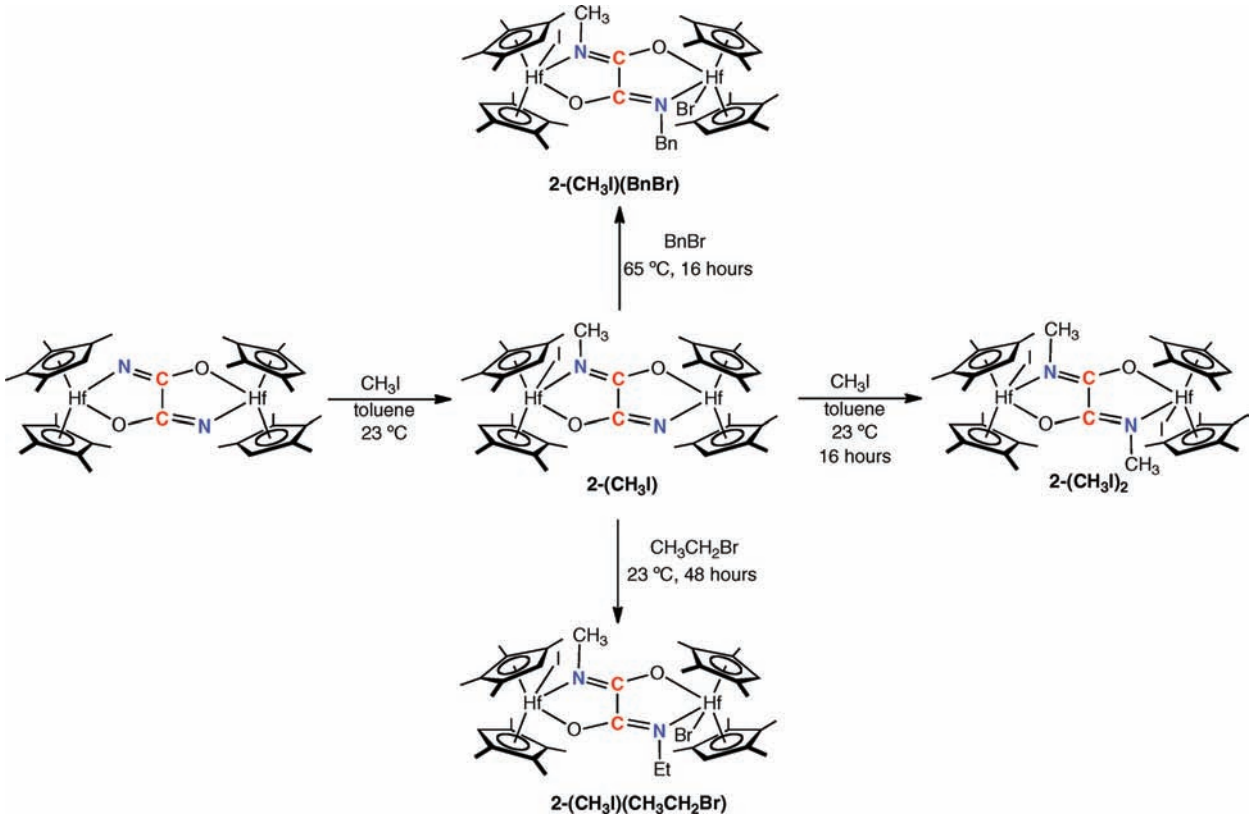
(40) Mindiola, D. J. *Acc. Chem. Res.* **2006**, *39*, 813.

(41) (a) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696. (b) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591. (c) Hoyt, H. M.; Michael, F. E.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 1018. (d) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

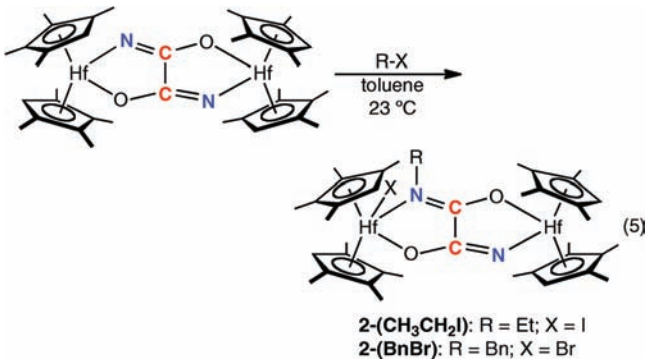
(42) Toomey, H. E.; Pun, D.; Veiros, L. F.; Chirik, P. J. *Organometallics* **2008**, *27*, 872.

(43) (a) Howard, W. A.; Trnka, T. M.; Waters, M.; Parkin, G. *J. Organomet. Chem.* **1997**, *528*, 95. (b) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4917.

Scheme 2. Methylation and Subsequent Alkylation of **2**



Complete assignment of the NMR data for both **2-(CH_2CH_3I)** and **2-(BnBr)** is reported in the Supporting Information.



The synthesis of monomethylated **2-(CH_3I)** prompted further alkylation studies, with the ultimate goal of synthesizing the *N*-monoalkyl- and *N*,*N*′-dialkyl-substituted oxamides in their free forms. Examples with equivalent and inequivalent alkyl substituents were targeted. Treatment of a toluene solution of **2-(CH_3I)** with either ethyl bromide or benzyl bromide resulted in alkylation of the remaining oxamidide nitrogen atom to furnish **2-(CH_3I)(CH_3CH_2Br)** or **2-(CH_3I)(BnBr)**, respectively (Scheme 2). In the case of benzyl bromide addition, heating the reaction mixture to 65 °C for approximately 16 h was required for complete conversion. NMR spectroscopic data for both **2-(CH_3I)(CH_3CH_2Br)** and **2-(CH_3I)(BnBr)** are reported in the Supporting Information and are fully consistent with a C_s dihafnium complex with inequivalent metallocene subunits arising from the formal 1,2-addition of the carbon−halogen bond.

Dimethylation of the oxamidide ligand was accomplished either by addition of a second equivalent of methyl iodide to **2-(CH_3I)** (Scheme 2) or by direct treatment of **2** with 2 equiv of CH_3I (eq 6). The latter procedure proved more convenient and yielded analytically pure iodohafnocene dimethyl oxamidate, **2-(CH_3I)$_2$**, in 92% yield. The formation of two N−CH_3 bonds via methylation of the hafnocene oxamidide was readily established by ^{1}H and ^{13}C NMR spectroscopy as the number of resonances consistent with a C_{2h}-symmetric dimeric hafnocene oxamidate complex was observed. Synthesis of **2-$^{15}N_2$-($^{13}CH_3I$)$_2$** was accomplished with $^{15}N_2$ gas and $^{13}CH_3I$, and analysis of the product by ^{13}C NMR spectroscopy established a $^1J_{C-N}$ of 4.3 Hz, consistent with N−C bond formation from the added methyl iodide. The solid-state structure of **2-(CH_3I)$_2$** was established by X-ray diffraction and a representation of the molecule is presented in Figure 5. Selected metrical parameters are presented in Table 1. Important features include the elongation of the Hf−N and Hf−O bonds, consistent with a change in the oxidation state of the core from $[N_2C_2O_2]^{4-}$ to

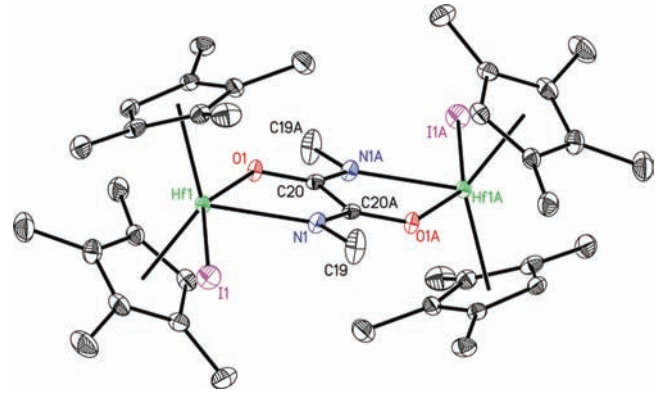
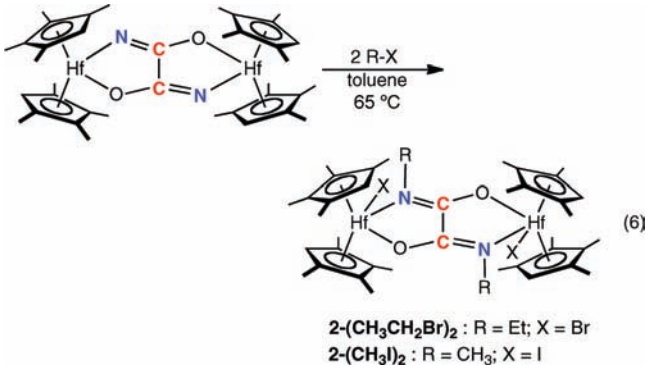


Figure 5. Representation of the solid-state structure of **2-(CH_3I)$_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

$[(NCH_3)_2C_2O_2]^{2-}$. Notably, the hafnium centers retain contact to both the oxygen and nitrogen and the C−N and C−O distances in the core are comparable to the values in the parent oxamidide **2**, suggesting only subtle geometrical changes in the overall transformation of **2** to **2-$(CH_3I)_2$**. The core of the molecule is essentially planar with a dihedral angle of 0.0°.

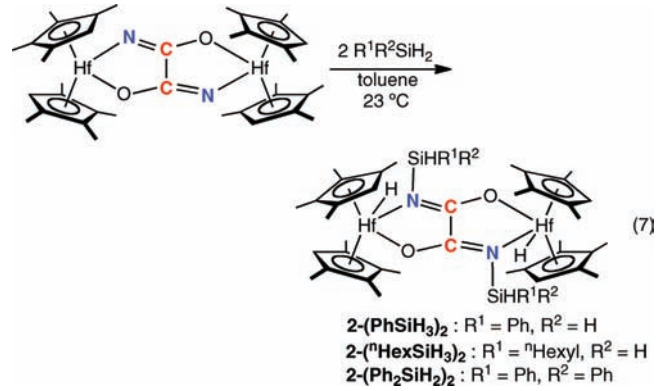
Similar dialkylations of **2** were accomplished by addition of ethyl bromide. In this manner, **2-$(CH_3CH_2Br)_2$** was synthesized in nearly quantitative yield after several days at room temperature or after 16 h at 65 °C (eq 6). As with the other halohafnocene oxamidate complexes, the NMR spectroscopic data establish two N−C bond-forming events and are reported in the Supporting Information. In contrast, addition of excess benzyl bromide to **2-(BnBr)** resulted in no further reaction up to 100 °C.



The alkylation of **2** with a series of alkyl halides prompted studies into releasing the functionalized core from the resulting hafnocene oxamidate compounds. We have previously reported that treatment of **1** (mixture of C_1 and C_2 isomers)[31] or **2**[32] with excess ethanol or anhydrous HCl released free oxamide, $H_2NC(O)$-$C(O)NH_2$, in nearly quantitative yield. On the basis of these results, the reactivity of each of the newly synthesized hafnocene oxamidate complexes with Brønsted acids was studied. A summary of these results is presented in Scheme 3. In each case, free *N*-monoalkyl or *N*,*N*′-dialkyl oxamides were liberated and their identities confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies. The products obtained from the dinitrogen functionalization studies were compared to materials prepared by independent synthesis or to previously reported data where possible (see Supporting Information).[44,45]

These *N*-monoalkyl- and *N*,*N*′- dialkyloxamides are known synthons for a variety of important small molecules and heterocycles (Scheme 3).[46−48] Importantly, the ease of ^{15}N and ^{13}C isotopic labeling into these complexes provides a convenient route to the small-scale synthesis of specifically labeled isotopologues of various *N*-containing small molecules and heterocycles. There is also considerable interest in the synthesis of substituted oxamides for their coordination properties, in particular their interesting electronic properties, when bound to late transition metals.[49]

Functionalization of Oxamidides with Silanes. The 1,2-addition reactivity of **2** with alkyl halides and the cycloaddition chemistry observed with **1** and heterocumulenes suggested that oxamidide functionalization may be possible with primary and secondary silanes. Additional motivation for these studies derives from Fryzuk's observation of dinitrogen functionalization[50] and cleavage upon addition of silanes.[18,19] Additional impetus was provided by our laboratory with the observation that dinitrogen carbonylation in the presence of primary silanes resulted in cleavage of the N≡N and C≡O bonds with release of free cyanosilanes.[32] Addition of a slight excess (2.2 equiv) of $PhSiH_3$ to a toluene solution of **2** and stirring the resulting mixture for 1 h at 23 °C, furnished a yellow solution from which a pale yellow solid identified as **2-$(PhSiH_3)_2$** was isolated in 86% yield (eq 7). At shorter reaction times, **2-$(PhSiH_3)_2$** was also the only new product observed by ^{1}H NMR spectroscopy. The benzene-d_6 ^{1}H NMR spectrum exhibits the number of peaks consistent with a C_{2h}-symmetric molecule arising from two 1,2-addition reactions of Si−H bonds across the hafnium−nitrogen bonds. A diagnostic hafnium hydride resonance was observed at 9.54 ppm. Similar idealized C_{2h}-symmetric silylated hafnocene oxamidate complexes were synthesized from addition of ^{n}HexylSiH$_3$ and Ph_2SiH_2 to **2** (eq 7). Complete spectroscopic details for both of these compounds are reported in the Supporting Information.



The solid-state structure of **2-$(PhSiH_3)_2$** was determined by X-ray diffraction. A representation of the molecule is presented in Figure 6 and selected bond distances are reported in Table 1. The data were of sufficient quality that the hafnium and silyl hydrides were located. The crystallographic data confirm Si−N bond formation and a disilylated oxamidate core. Similar to **2-$(CH_3I)_2$**, the Hf−O and Hf−N bonds in **2-$(PhSiH_3)_2$** are slightly elongated with respect to the parent oxamidide, **2**, consistent with oxamidate ($[(NSiH_2Ph)_2C_2O_2]^{2-}$) formation. The Hf−H bond is comparable with those reported previously in related compounds.[32] The oxamidate core is essentially planar, and the dihedral angle between hafnocene subunits is 24.1°.

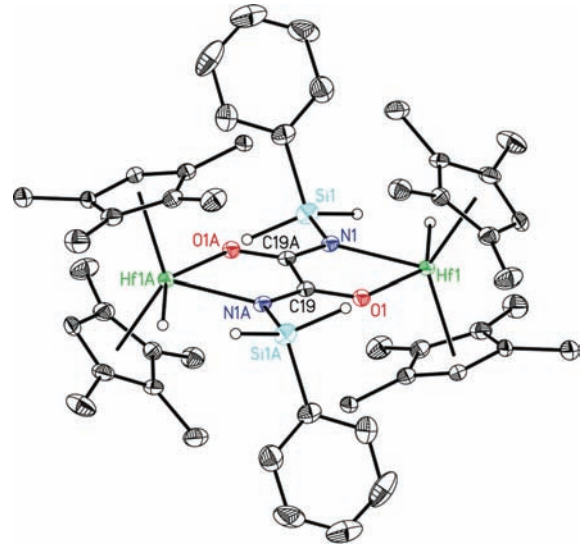
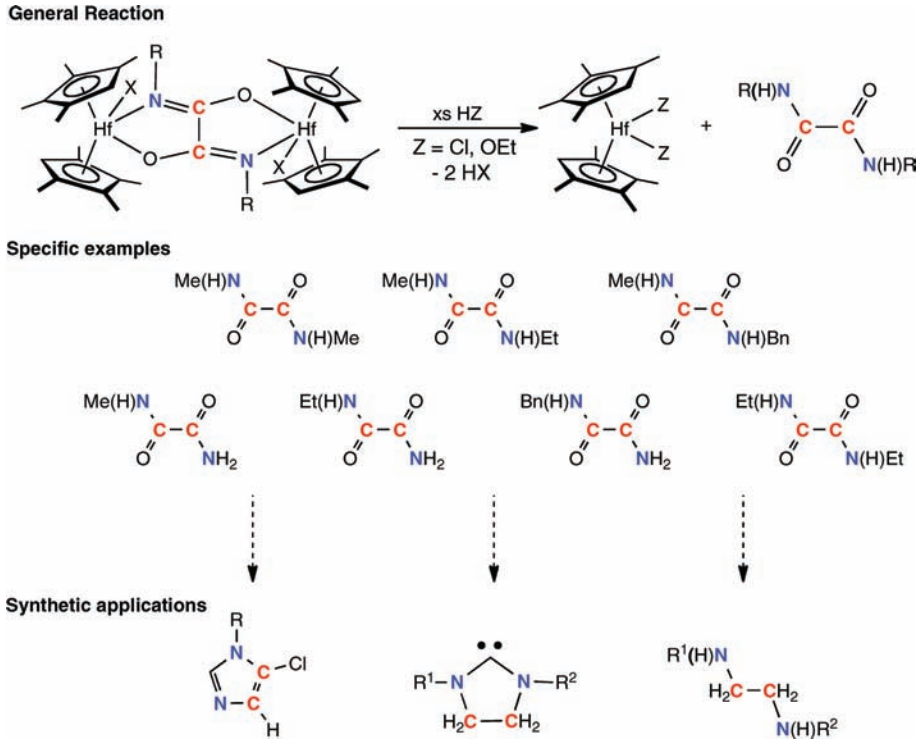
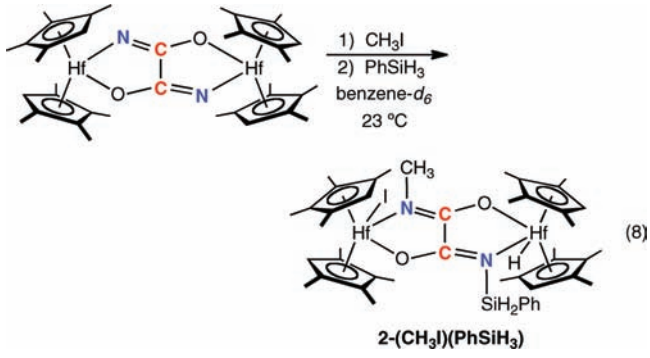


Figure 6. Representation of the solid-state structure of **2-$(PhSiH_3)_2$** at 30% probability ellipsoids. Hydrogen atoms, except for the hafnium and silyl hydrides, are omitted for clarity.

Scheme 3. Synthesis of Free *N*-Monosubstituted and *N*,*N*′-Disubstituted Oxamides



Functionalization of the oxamidide core in **2** with both alkyl halides and silanes prompted exploration of a combined strategy where additional nitrogen−element bond formation was accomplished with both reagent types. The monomethylated complex, **2-(CH$_3$I)**, was prepared *in situ* in benzene-d_6 followed by addition of 1.2 equiv of $PhSiH_3$. Complete conversion to **2-(CH$_3$I)(PhSiH$_3$)** was observed immediately (eq 8). Characterization of **2-(CH$_3$I)(PhSiH$_3$)** by ^{1}H and ^{13}C NMR spectroscopy was diagnostic of both methyl iodide and silane addition to the oxamidide core. The benzene-d_6 ^{1}H NMR spectrum exhibited the number of peaks consistent with formation of two inequivalent metallocene subunits along with a diagnostic Hf−H resonance at 9.38 ppm. The new N−CH_3 group was located at 3.67 ppm ($^3J_{C-H}$ = 4.4 Hz), while the Si−H resonance for the newly formed N−Si bond was assigned at 4.89 ppm. The benzene-d_6 ^{13}C NMR spectrum also exhibited diagnostic peaks for an oxamidate core functionalized with two different groups. Inequivalent carbons were observed at 170.33 and 173.05 ppm ($^1J_{C-C}$ = 72.5 Hz). In addition, C=N and Si−H bands were observed at 1558 and 2119 cm^{-1}, respectively, in the solid-state (KBr) infrared spectrum.



(8)

Concluding Remarks

Methods for the functionalization of hafnocene oxamidide cores, prepared from CO-induced N_2 bond cleavage, were discovered that exploit the nucleophilicity and basicity of the hafnium−nitrogen bonds. For the *ansa*-hafnocene, **1**, cycloaddition of heterocumulenes such as ^{t}BuNCO and CO_2 resulted in additional N−C bond assembly with concomitant formation of hafnium−oxygen bonds. The latter functionalization reaction demonstrates that organic molecules, in the form of a coordinated ligand, can be synthesized from three abundant and often inert small molecules: N_2, CO, and CO_2. For **2**, sequential 1,2-addition of alkyl halides was observed resulting in the synthesis of, following protonolysis, free *N*,*N*′-disubstituted oxamides that are useful precursors for the preparation of *N*,*N*′-diamines, *N*-heterocylic carbenes, and various heterocycles. Given the availability of ^{13}CO and $^{15}N_2$, isotopically labeled variants of these molecules are also synthetically accessible. In addition to alkyl halides, elaboration of the hafnocene oxamidides was also accomplished with primary and secondary silanes and terminal alkynes. DFT studies established Hf−N multiple bond character in the hafnium oxamidide core, with nucleophilic and basic nitrogen atoms that facilitate alkylation with alkyl halides, silylation with organosilanes, and C−H bond activation of terminal alkynes.

Experimental Section[51]

Preparation of ([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Hf)$_2$(^{t}BuNCO)$_2$($N_2C_2O_2$) (1-(^{t}BuNCO)$_2$). In a drybox, a 20 mL scintillation vial was charged with 0.090 g (0.087 mmol) of **1-C$_2$** in approximately 10 mL of toluene. An excess of *tert*-butylisocyanate

(44) Desseyn, H. O.; Perlepes, S. P.; Clou, K.; Blaton, N.; Van der Veken, B. J.; Dommisse, R.; Hansen, P. E. *J. Phys. Chem. A* **2004**, *108*, 5175.
(45) Pfoertner, K.; Daly, J. J. *Helv. Chim. Acta* **1987**, *70*, 171.
(46) Blicke, F. F.; Godt, H. C. *J. Am. Chem. Soc.* **1954**, *76*, 3653.
(47) Denk, M. K.; Hezarkhani, A.; Zheng, F. *Eur. J. Inorg. Chem.* **2007**, 3527.
(48) Lambert, J. B.; Huseland, D. E.; Wang, G. *Synthesis* **1986**, 657.
(49) Ruiz, R.; Faus, J.; Lloret, F.; Julve, M.; Journaux, Y. *Coord. Chem. Rev.* **1999**, *193*, 1069.
(50) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.

(50 μL, 0.44 mmol) was added via syringe, and the reaction was stirred for 2 h at ambient temperature. After this time, the solvent and excess isocyanate were removed *in vacuo*, and the resulting orange oil was washed with pentane to yield a pale yellow solid which was purified via recrystallization from a minimal amount of diethyl ether, furnishing pale yellow crystals of **1-(^{t}BuNCO)$_2$** in 56% yield. ^{1}H NMR (benzene-d_6): δ = 0.52 (s, 6H, SiMe_2), 0.58 (s, 6H, SiMe_2), 1.41 (s, 18H, C_5H_3C*Me*$_3$), 1.68 (s, 18H, *Me*$_3$CNCO), 1.85 (s, 6H, C_5*Me*$_4$), 1.88 (s, 6H, C_5*Me*$_4$), 2.07 (s, 6H, C_5*Me*$_4$), 2.31 (s, 6H, C_5*Me*$_4$), 5.35 (m, 2H, C_5H_3CMe$_3$), 5.62 (m, 2H, C_5H_3CMe$_3$), 6.27 (m, 2H, C_5H_3CMe$_3$). {^{1}H}^{13}C NMR (benzene-d_6): δ = −0.65 (SiMe_2), −0.83 (SiMe_2), 11.21 (Cp*Me*), 11.89 (Cp*Me*), 14.10 (Cp*Me*), 14.30 (Cp*Me*), 31.85 (CpC*Me*$_3$), 32.63 (*Me*$_3$CNCO), 33.55 (Cp*C*Me$_3$), 55.54 (Me$_3$*C*NCO), 103.28, 109.62, 109.91, 117.86, 121.42, 122.09, 122.90, 129.67, 133.41, 147.32 (*Cp*), 147.55 (Me$_3$CN*C*O), N$_2$(^{t}BuNCO)$_2$$C_2O_2$ not located. IR (KBr): ν = 1647, 1673 cm^{-1} (C═N).

Preparation of ([Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Hf)$_2$(CO$_2$)$_2$-(N$_2$C$_2$O$_2$) (1-(CO$_2$)$_2$). In a drybox, a thick-walled glass vessel was charged with 0.130 g (0.13 mmol) of **1-*C*$_2$** and approximately 10 mL of toluene. On a high-vacuum line, the vessel was submerged in liquid nitrogen and degassed, and 2.2 equiv of carbon dioxide were added to the reaction vessel via a calibrated gas bulb (50.8 Torr, 100.1 mL). The contents of the vessel were thawed and stirred for 1 h, after which time excess carbon dioxide and solvent were removed *in vacuo*. The vessel was transferred into a drybox, and the resulting yellow oil was washed with cold pentane, furnishing 0.124 g (88%) of a yellow solid identified as **1-(CO$_2$)$_2$**. Anal. Calcd for $C_{44}H_{60}O_6N_2Si_2Hf_2$: C, 49.76; H, 5.69; N, 2.64. Found: C, 50.06; H, 5.67; N, 2.28. ^{1}H NMR (benzene-d_6): δ = 0.48 (s, 6H, SiMe_2), 0.51 (s, 6H, SiMe_2), 1.37 (s, 18H, C_5H_3C*Me*$_3$), 1.62 (s, 6H, C_5*Me*$_4$), 1.76 (s, 6H, C_5*Me*$_4$), 1.97 (s, 6H, C_5*Me*$_4$), 2.01 (s, 6H, C_5*Me*$_4$), 5.38 (m, 2H, C_5H_3CMe$_3$), 5.57 (m, 2H, C_5H_3CMe$_3$), 6.25 (m, 2H, C_5H_3CMe$_3$). {^{1}H}^{13}C NMR (benzene-d_6): δ = −0.54 (SiMe_2), 0.17 (SiMe_2), 10.69 (Cp*Me*), 11.64 (Cp*Me*), 13.90 (Cp*Me*), 14.06 (Cp*Me*), 31.31 (C*Me*$_3$), 34.09 (*C*Me$_3$), 102.94, 108.61, 110.13, 111.70, 119.16, 119.29, 119.45, 122.64, 128.68, 129.95 (*Cp*), 150.54 (N$_2$(*C*O$_2$)$_2$C$_2$O$_2$) ($^2J_{CC}$ = $^3J_{CC}$ = 1.5 Hz, reported as an average[36]), 163.18 (N$_2$(CO$_2$)$_2$*C*$_2$O$_2$). IR (KBr): ν = 1637 cm^{-1} (C═N), 1734 cm^{-1} (C═O).

Preparation of [Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-^{t}Bu)]Hf(I)(NCO) (1-(I)(NCO)). In a drybox, a 20 mL scintillation vial was charged with 0.057 g (0.055 mmol) of **1** (mixture of C_1 and C_2 isomers) dissolved in approximately 10 mL of toluene. A solution containing 0.015 g (0.059 mmol) of iodine in approximately 5 mL of toluene was added dropwise over about 1 min with stirring. After 1 h, the solvent and the unreacted iodine were removed *in vacuo*. The remaining yellow residue was washed with pentane to furnish 0.065 g (92%) of a pale yellow solid identified as **1-(I)(NCO)**. The reaction was conveniently performed on the NMR scale, enabling the synthesis and characterization of the ^{15}N and ^{13}C isotopologues, **(1-(I)(N^{13}CO)** and **1-(I)(^{15}N^{13}CO))**. Anal. Calcd for $C_{19}H_{26}N_1O_1I_1Hf_1$: C, 38.69; H, 4.44; N, 2.38. Found: C, 38.92; H, 4.45; N, 2.24. ^{1}H NMR (benzene-d_6): δ = 0.31 (s, 3H, SiMe_2), 0.36 (s, 3H, SiMe_2), 1.31 (s, 9H, C_5H_3C*Me*$_3$), 1.58 (s, 3H, C_5*Me*$_4$), 1.64 (s, 3H, C_5*Me*$_4$), 1.84 (s, 3H, C_5*Me*$_4$), 2.31 (s, 3H, C_5*Me*$_4$), 5.10 (m, 1H, C_5H_3CMe$_3$), 5.37 (m, 1H, C_5H_3CMe$_3$), 7.25 (m, 1H, C_5H_3CMe$_3$). {^{1}H}^{13}C NMR (benzene-d_6): δ = −0.43 (SiMe_2), −0.25 (SiMe_2), 11.89 (Cp*Me*), 15.08 (Cp*Me*), 15.54 (Cp*Me*), 15.90 (Cp*Me*), 31.20 (C*Me*$_3$), 33.42 (*C*Me$_3$), 98.39, 104.58, 105.39, 108.12, 111.81, 121.95, 123.39, 125.60, 133.51, 149.73 (*Cp*), 136.81 (N*C*O) ($^1J_{NC}$ = 33.0 Hz). IR (KBr): ν = 2229 cm^{-1} (NCO).

Preparation of [(η^5-C$_5$Me$_4$H)$_2$Hf]$_2$(CCPh)$_2$((NH)$_2$C$_2$O$_2$) (2-(PhCCH)$_2$). A J. Young NMR tube was charged with 0.015 g (0.016 mmol) of **2** and approximately 0.5 mL of benzene-d_6. A slight excess of phenylacetylene (2.2 equiv, 0.035 mmol) was added via syringe, and the resulting reaction mixture was shaken and heated at 65 °C for 1 h. After this time, complete conversion to **2-(PhCCH)$_2$** was observed, as judged by ^{1}H NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ = 1.75 (s, 12H, CpMe_4H), 2.06 (s, 12H, CpMe_4H), 2.10 (s, 12H, CpMe_4H), 2.12 (s, 12H, CpMe_4H), 5.09 (s, 4H, CpMe$_4$*H*), 6.66 (s, 2H, N*H*), 7.10−7.15 (m, 6H, CC*Ph*), 7.55−7.60 (m, 4H, CC*Ph*). {^{1}H}^{13}C NMR (benzene-d_6): δ = 12.38, 13.14, 13.94, 14.48 (Cp*Me*), 95.01 (*CC*Ph), 110.29, 114.47, 114.90, 117.42, 120.75, 122.12, 126.25, 128.27, 128.88, 131.49, 132.73 (*Cp* and CC*Ph*), 171.34 ((NH)$_2$*C*$_2$O$_2$), 1 *CC*Ph not found. IR (KBr): ν = 2087 cm^{-1} (CC), 3371 cm^{-1} (NH).

Preparation of [(η^5-C$_5$Me$_4$H)$_2$Hf]$_2$(I)(N(CH$_3$)NC$_2$O$_2$) (2-(CH$_3$I)). In a drybox, a 100 mL round-bottom flask was charged with 0.100 g (0.11 mmol) of **2** and 20 mL of toluene. A 180° needle valve was attached, and the contents of the assembly were degassed on a high-vacuum line. While the contents were frozen at liquid nitrogen temperature, 23.9 Torr of CH_3I was added via a 100.1 mL calibrated gas bulb. The contents of the flask were warmed to ambient temperature and stirred for 1 h. The excess methyl iodide and solvent were removed *in vacuo*, and the flask was transferred into the drybox. The resulting yellow oil was washed with cold pentane and furnished 0.093 g (81%) of a yellow solid, identified as **2-(CH$_3$I)**. ^{1}H NMR (benzene-d_6): δ = 1.66 (s, 6H, CpMe_4H), 1.67 (s, 6H, CpMe_4H), 1.73 (s, 6H, CpMe_4H), 1.95 (s, 6H, CpMe_4H), 2.06 (s, 6H, CpMe_4H), 2.22 (s, 6H, CpMe_4H), 2.44 (s, 6H, CpMe_4H), 2.48 (s, 6H, CpMe_4H), 2.49 (s, 3H, NCH_3), 5.50 (s, 2H, CpMe$_4$*H*), 5.55 (s, 2H, CpMe$_4$*H*). {^{1}H}^{13}C NMR (benzene-d_6): 11.24 (Cp*Me*), 12.18 (Cp*Me*), 13.01 (Cp*Me*), 13.26 (Cp*Me*), 13.36 (Cp*Me*), 14.75 (Cp*Me*), 14.88 (Cp*Me*), 15.96 (Cp*Me*), 31.58 (N*CH*$_3$) ($^1J_{CN}$ = 5.3 Hz, $^2J_{CC}$ = 3.0 Hz, $^3J_{CC}$ = 1.8 Hz), 109.60, 112.29, 114.61, 117.37, 118.19, 120.85, 123.07, 123.56, 126.95 (*Cp*), 161.12 (N(CH$_3$)(*C*O)NCO), 173.31 (N(CH$_3$)(CO)N*C*O) ($^1J_{CC}$ = 75.3 Hz), 1 *Cp* resonance not located. IR (KBr): ν = 1618 cm^{-1} (C═N).

Preparation of ((η^5-C$_5$Me$_4$H)$_2$Hf)$_2$(I)$_2$(N$_2$(CH$_3$)$_2$C$_2$O$_2$) (2-(CH$_3$I)$_2$). In a drybox, a thick-walled glass vessel was charged with 0.120 g (0.13 mmol) of **2** and approximately 20 mL of toluene. On a high-vacuum line, the vessel was degassed, and 59.8 Torr of methyl iodide was added via a 100.1 mL calibrated gas bulb. The contents of the vessel were thawed and stirred at 65 °C for 16 h. After this time, the excess methyl iodide and solvent were removed *in vacuo*. The vessel was transferred into the drybox and the resulting yellow oil washed with cold pentane to furnish 0.144 g (92%) of a yellow solid, identified as **2-(CH$_3$I)$_2$**. Anal. Calcd for $C_{40}H_{58}O_2N_2I_2Hf_2$: C, 39.71; H, 4.83; N, 2.32. Found: C, 39.98; H, 4.90; N, 2.29. ^{1}H NMR (benzene-d_6): δ = 1.55 (s, 12H, CpMe_4H), 1.86 (s, 12H, CpMe_4H), 2.12 (s, 12H, CpMe_4H), 2.15 (s, 12H, CpMe_4H), 3.58 (s, 6H, NCH_3), 5.40 (s, 4H, CpMe$_4$*H*). {^{1}H}^{13}C NMR (benzene-d_6): δ = 12.14 (Cp*Me*), 14.52 (Cp*Me*), 15.12 (Cp*Me*), 16.32 (Cp*Me*), 45.50 (N*CH*$_3$) ($^1J_{CN}$ = 4.3 Hz), 112.62, 116.07, 120.08, 122.43, 127.50 (*Cp*), 167.94 (N$_2$(CH$_3$)$_2$*C*$_2$O$_2$). IR (KBr): ν = 1606 cm^{-1} (C═N).

Preparation of [(η^5-C$_5$Me$_4$H)$_2$Hf]$_2$(H)$_2$((NSiH$_2$Ph)$_2$C$_2$O$_2$) (2-(PhSiH$_3$)$_2$). In a drybox, a 20 mL scintillation vial was charged with 0.100 g (0.11 mmol) of **2** and approximately 10 mL of toluene. Via syringe, 2.2 equiv (0.029 mL, 0.24 mmol) of phenylsilane was added with stirring. Once the addition was complete, the resulting reaction mixture was stirred for 1 h at 23 °C, after which time excess phenylsilane and solvent were removed *in vacuo*. The resulting yellow oil was washed with cold pentane, furnishing 0.106 g (86%) of a pale yellow solid, identified as **2-(PhSiH$_3$)$_2$**. The product was recrystallized from toluene at −35 °C and isolated as pale yellow crystals. Anal. Calcd for $C_{50}H_{68}O_2N_2Si_2Hf_2$: C, 52.57; H, 6.00; N, 2.45. Found: C, 52.36; H, 5.80; N, 2.40. ^{1}H NMR (benzene-d_6): δ = 1.72 (s, 12H, CpMe_4H), 1.84 (s, 12H, CpMe_4H), 2.09 (s, 24H, CpMe_4H, 2 coincident), 4.93 (s, 4H, NSiCH_2Ph), 5.81 (s, 4H, CpMe$_4$*H*), 7.22−7.33 (m, 6H, NSiCH$_2$*Ph*), 8.09 (d, 4H, NSiCH$_2$*Ph*), 9.54 (s, 2H, Hf*H*). {^{1}H}^{13}C NMR (benzene-d_6): δ =

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

12.25 (Cp*Me*), 12.72 (Cp*Me*), 13.74 (Cp*Me*), 15.19 (Cp*Me*), 107.69, 111.78, 115.57, 118.17, 120.50 (*Cp*), 128.26, 130.49, 136.65, 137.95 (SiH_2*Ph*), 175.37 ($N_2(SiCH_2Ph)_2C_2O_2$). IR (KBr): $\nu = 1552$ cm^{-1} (C═N), 2157 cm^{-1} (SiH_2).

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Supporting Information Available: General experimental considerations, additional procedures, computational details, and representative NMR spectra; crystallographic data for **1-(^{t}BuNCO)$_2$**, **1-(CO$_2$)$_2$**, **1-(I)(NCO)**, **2-(CH$_3$I)$_2$**, and **2-(PhSiH$_3$)$_2$** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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