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Structure and Reactivity of a Hafnocene μ-Nitrido Prepared From Dinitrogen Cleavage[**]

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The six-electron cleavage of molecular nitrogen by soluble metal complexes to form either terminal[1] or bridging nitrido[2] compounds is an attractive transformation for developing synthetic routes to organic molecules using N_2 as the nitrogen source.[3] Acylation,[4] silylation,[5] alkylation[6] and hydrogenation[7] have all been identified as viable strategies to construct new bonds to metal–nitrido complexes following N_2 cleavage. Despite numerous examples in Groups 5 and 6, to our knowledge, a Group 4 transition metal nitrido complex has not been isolated following N_2 cleavage. Examples of nitrido clusters of this triad have been synthesized using ammonia as the N-atom source with hafnium being a notable exception.[8] Here we describe the synthesis, structural characterization, and electronic structure determination of hafnocene μ-nitrido complexes prepared from CO-induced dinitrogen cleavage and evaluate their intermediacy in N–C bond forming reactions.

CO-induced N_2 cleavage has recently emerged as a particularly effective strategy for the formation of N–C and C–C bonds from zirconocene and hafnocene dinitrogen complexes with activated N_2 ligands (Figure 1).[9,10] Computational[11] and recent experimental[12] studies into the mechanism of N_2 carbonylation with the *ansa*-hafnocene dinitrogen complex, $[\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}t\text{Bu})Hf\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$, support formation of a μ-nitrido intermediate although the reactivity of the compound has precluded experimental observation. C–H activation by 1,2-addition of a *tert*-butyl substituent occurs in the absence of excess carbon monoxide[10a] and the putative dihafnocene μ-nitrido has been intercepted with dihydrogen[10b] and terminal alkynes[10b] as predicted computationally.[11]

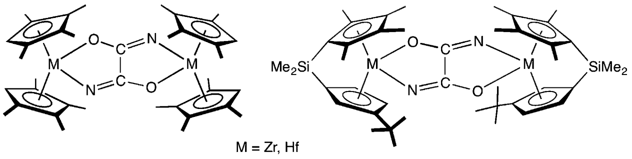
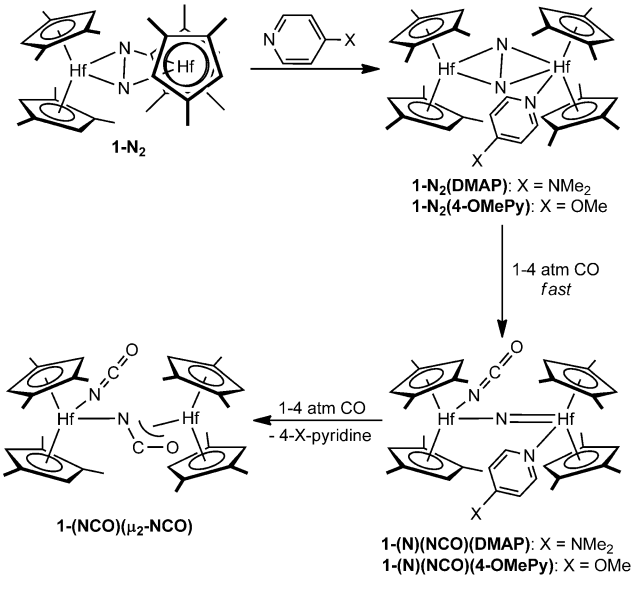


Figure 1. Zirconocene and hafnocene oxamidide complexes prepared from CO-induced N_2 cleavage.

In an attempt to eliminate competing intramolecular cyclometalation chemistry, CO-induced N_2 bond cleavage was studied with the less sterically protected hafnocene dinitrogen complex, $[\{(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ (**1-N_2**).[13] This compound has an identical N–N bond distance of 1.457(5) Å to the *ansa*-hafnocene, $[\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}t\text{Bu})Hf\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$, yet exhibits unique N_2 functionalization and cleavage chemistry that has been ascribed to the accessibility of bimetallic species due to the less encumbering cyclopentadienyl rings.[13] Because our previous studies established the role of a terminal CO ligand during the course of oxamidide formation with the *ansa*-hafnocene, experiments were conducted in the presence of neutral donors. Addition of 4-(dimethylamino)pyridine (DMAP) to a diethyl ether solution of **1-N_2** immediately produced an ink green solution, which following recrystallization at −35 °C, afforded dark green crystals identified as the DMAP adduct of the hafnocene dinitrogen compound, $[\{(\eta^5\text{-}C_5H_2\text{-}1,2,4\text{-}Me_3)_2Hf\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)](\text{DMAP})$ (**1-N_2(DMAP)**, Scheme 1).

The solid-state structure of **1-N_2(DMAP)** (Figure 2) establishes that the side-on hapticity of the dinitrogen ligand is retained upon DMAP coordination. This contrasts the behavior of related zirconocene dinitrogen complexes



Scheme 1.

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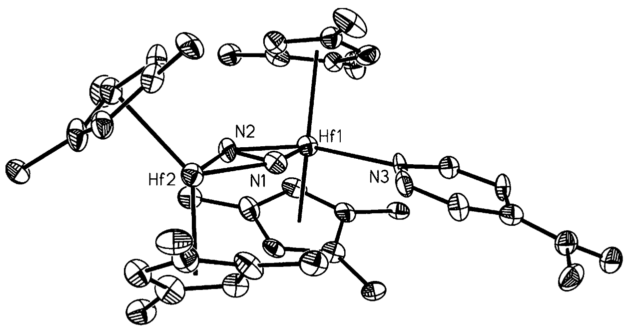


Figure 2. Representation of the solid state structure of **1-N$_2$(DMAP)** at 30% probability ellipsoids.[16] Hydrogen atoms omitted for clarity. Selected bond lengths [Å]: N1–N2 1.39(2), Hf1–N1 2.100(15), Hf2–N1 2.066(16), Hf1–N2 2.109(13), Hf2–N2 2.091(14), Hf1–N3 2.375(15).

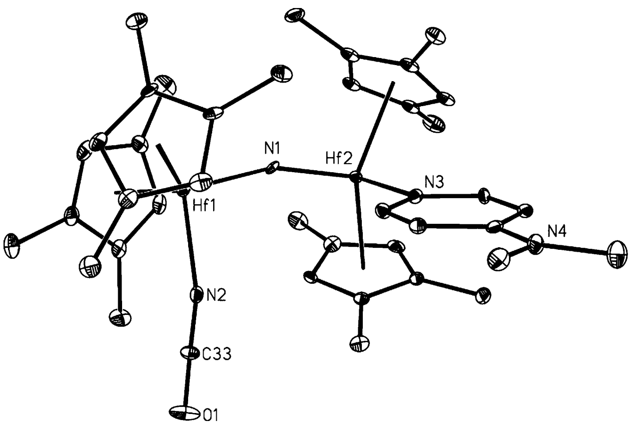


Figure 3. Representation of the solid state structure of **1-(N)(NCO)(DMAP)** at 30% probability ellipsoids.[16] Hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Hf1–N1 1.971(4), Hf2–N1 1.937(4), Hf1–N2 2.149(4), Hf2–N3 2.278(5).

where isomerization of the side-on (η^2,η^2-N$_2$) to end-on (η^1,η^1-N$_2$) accompanies ligand coordination and highlights the benefits of the less sterically protected hafnocenes.[14] The N–N bond distance of 1.39(2) Å is contracted compared to the value found in **1-N$_2$** and is likely a consequence of the lengthening of the Hf–Hf distance to 3.9406(13) Å (from 3.8527(3) in **1-N$_2$**) reducing overlap of the metal with the N$_2$ π^* molecular orbitals. DFT calculations also support this view as the HOMO (Supporting Information, Figure S1) exhibits back-bonding only from the base-free hafnium.

The [D$_6$]benzene ^{1}H NMR spectrum of **1-N$_2$(DMAP)** exhibits broad resonances at 23 °C, consistent with DMAP dissociation and recoordination on the timescale of the experiment. Cooling a [D$_8$]toluene solution to −10 °C produced sharper peaks, the number of which is consistent with a bimetallic compound with inequivalent hafnocene subunits. Accordingly, the ^{15}N NMR spectrum of **1-N$_2$(DMAP)** exhibits two doublets ($^1J_{\text{N-N}} = 21.2$ Hz) centered at 449.93 and 466.60 ppm (Figure S2).

Exposure of a toluene solution of **1-N$_2$(DMAP)** to excess carbon monoxide, typically 1–4 atm, resulted in rapid formation of a red solution from which the μ-nitrido dihafnocene isocyanate DMAP complex, [{(η^5-C$_5$H$_2$-1,2,4-Me$_3$)$_2$Hf}$_2$(μ_2-N)(NCO)(DMAP)] (**1-(N)(NCO)(DMAP)**), was isolated as a yellow solid in 57% yield following recrystallization from a pentane–toluene mixture (Scheme 1). The [D$_6$]benzene solution IR spectrum exhibits a strong band centered at 2219 cm^{-1} which shifts appropriately to 2148 cm^{-1} when the synthesis is performed with ^{15}N$_2$ and ^{13}CO, diagnostic of a terminal isocyanate ligand from CO-induced N$_2$ cleavage.[10] The benzene ^{1}H and ^{13}C NMR spectra exhibit the number of resonances for a bimetallic compound with two distinct hafnocene subunits, one of which contains a coordinated pyridine ligand. Additional evidence for N$_2$ cleavage and μ-nitrido formation was provided by ^{15}N NMR spectroscopy on the ^{15}N, ^{13}C isotopologue, **1-(^{15}N)(^{15}N ^{13}CO)(DMAP)** (Figure S3). A doublet ($^1J_{\text{C-N}} = 32.2$ Hz) was observed at 88.53 ppm for the terminal [NCO] ligand while a sharp singlet was located at 567.19 ppm for the μ-nitrido.

The structure of **1-(N)(NCO)(DMAP)** was also determined by X-ray diffraction and a representation of the molecular structure is presented in Figure 3. The bond distances to the formally μ_2-[N]$^{3-}$ are slightly asymmetric as the Hf1–N1 bond of 1.971(4) Å is longer than the Hf2–N1 bond of 1.937(4). The latter bond is also longer than expected for a hafnocene imido compound and suggests a reduction in bond order. To our knowledge, this is the first isolation and structural characterization of a hafnium μ-nitrido compound and a rare example of an isolable Group 4 transition metal nitrido compound prepared from N$_2$ cleavage.

Isolation of pure **1-(N)(NCO)(DMAP)** was often frustrated by cocrystallization with free DMAP. To alleviate this complication and to study the scope of the transformation, reactions with other pyridines were explored. Addition of 4-OMe-pyridine to a [D$_6$]benzene solution of **1-N$_2$** resulted in a broadening of the ^{1}H NMR resonances of the parent compound, suggesting reversible formation of **1-N$_2$(4-OMePy)**. Attempts to isolate this compound in the solid state were unsuccessful, likely due to the reduced basicity of 4-OMe-pyridine relative to DMAP. Attempts to carbonylate **1-N$_2$** in the presence of pyridine led to the formation of a complex mixture of unidentified products.

Carbonylation of a toluene solution of **1-N$_2$** in the presence of 4-OMe-pyridine furnished the expected μ-nitrido dihafnocene isocyanate complex, **1-(N)(NCO)(4-OMePy)**. The solid-state structure (Figure 4) and spectroscopic properties (see Supporting Information) are comparable to **1-(N)(NCO)(DMAP)**. To gain insight into the electronic structure and bonding in the μ-nitrido hafnocene complex, full molecule DFT calculations were performed on **1-(N)(NCO)(4-OMePy)**. The computational results successfully reproduced the experimentally established geometry and metrical parameters (see Supporting Information). An illustration of the DFT-computed HOMO is presented in Figure 5. Notably, this molecular orbital is principally μ-nitrido based and indicates little multiple bond character with the hafnium centers, consistent with the Hf–N bond distances measured crystallographically. The computational results establish that a zwitterionic resonance structure with reduced hafnium–nitrogen π-back-bonding is the more accurate representation of the molecule (Scheme 2).

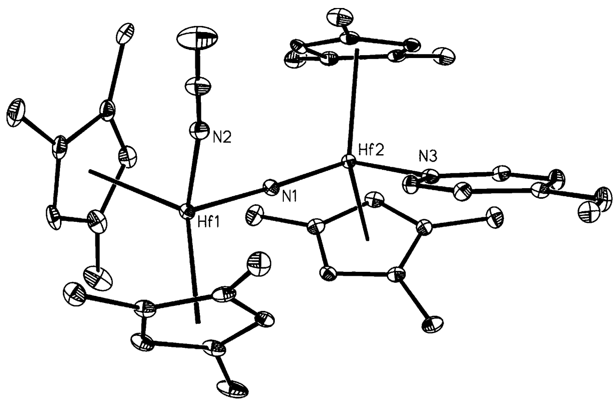


Figure 4. Representation of the solid state structure of **1-(N)(NCO)-(4-OMePy)** at 30% probability ellipsoids.[16] Hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Hf1–N1 1.968(4), Hf2–N1 1.933(4), Hf1–N2 2.144(4), Hf2–N3 2.309(5).

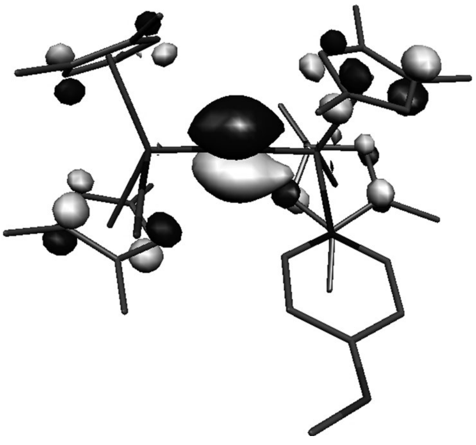
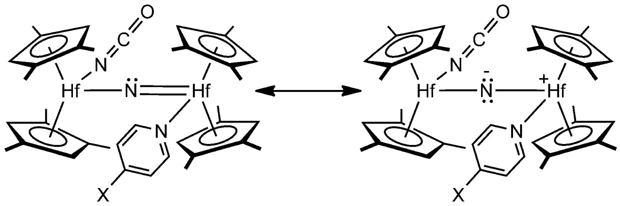


Figure 5. Illustration of the DFT-computed HOMO of **1-(N)(NCO)-(4-OMePy)**.

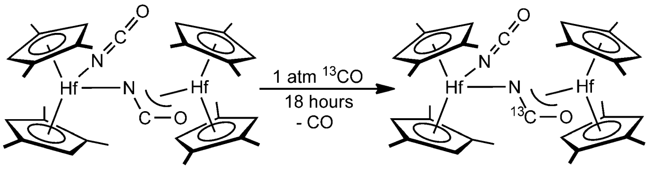


Scheme 2.

The synthesis and isolation of μ-nitrido hafnocene complexes from CO-induced N_2 cleavage prompted exploration of additional carbonylation chemistry and evaluation of their possible intermediacy in C–C coupling and oxamide formation. Exposure of a toluene solution of **1-(N)(NCO)-(4-OMePy)** to 4 atm of CO for 18 h followed by solvent removal and washing with cold pentane furnished a white solid identified as the dihafnocene isocyanate complex, **1-(NCO)(μ_2-NCO)**, in 77% yield (Scheme 1). Monitoring the reaction by ^{1}H NMR spectroscopy revealed that loss of one equivalent of free 4-OMe-pyridine accompanied the carbonylation reaction.

The [D$_6$]benzene ^{1}H NMR spectrum of **1-(NCO)(μ_2-NCO)** exhibited the number of cyclopentadienyl resonances expected for a C_s symmetric bimetallic compound. The ^{15}N NMR spectrum of **1-(^{15}N^{13}CO)(μ_2-^{15}N^{13}CO)** contains two doublets—one centered at 94.15 ppm ($^1J_{N\text{-}C} = 32.8$ Hz) diagnostic of a terminal hafnocene isocyanate and a second peak at 324.15 ppm ($^1J_{N\text{-}C} = 8.3$ Hz) assigned as a bridging isocyanate. Accordingly, two doublets were observed by ^{13}C NMR spectroscopy at 135.4 and 164.1 ppm for the terminal and bridging isocyanates, respectively. Formation of these ligands[15] from nitrido carbonylation was also confirmed by infrared spectroscopy. Two strong bands centered at 2223 and 2203 cm^{-1} are observed in the [D$_6$]benzene solution IR spectrum. These bands shift appropriately to 2148 and 2138 cm^{-1}, respectively, in the ^{15}N/^{13}C labeled isotopologue. Representative spectra are presented in the Supporting Information. The recently identified intermediate in oxamidide formation, [{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$-3-*t*Bu)Hf}$_2$(μ-NCO)(CO)(NCO)],[12] is, to our knowledge, the only other hafnocene with a bridging isocyanate ligand. The ^{15}N NMR spectrum of the ^{15}N/^{13}CO isotopologue of this compound exhibits a doublet ($^1J_{CN} = 9.6$ Hz) at 241.14 ppm and a ^{13}C resonance at 192.5 ppm in [D$_6$]benzene. The discrepancies in chemical shifts between the *ansa*-hafnocene compound and **1-(NCO)(μ_2-NCO)** are likely a result of CO coordination in the former.

The reversibility of μ-nitrido carbonylation was explored with the ^{13}C labeling experiment outlined in Scheme 3. A [D$_6$]benzene solution of **1-(NCO)(μ_2-NCO)** was exposed to 1 atm of ^{13}CO gas for 18 h. Monitoring the reaction by ^{13}C NMR spectroscopy revealed the incorporation of the isotopic label into the carbon at 164.1 ppm. No enrichment of the terminal isocyanate was observed even after extended periods under ^{13}CO as evidenced by the lack of enhancement of the resonance at 135.4 ppm. Infrared spectroscopic analysis of the ^{13}C-isotopologue, **1-(NCO)(μ_2-N^{13}CO)**, displayed the expected strong band at 2223 cm^{-1} for the natural abundance terminal isocyanate and a new band at 2163 cm^{-1} for the ^{13}C-labeled bridging isocyanate, in good agreement with a simple harmonic oscillator model (2157 cm^{-1}). These observations established reversible N–C bond formation through insertion of CO into the bridging nitrido fragment but not into the terminal isocyanate. Furthermore, allowing [D$_6$]benzene solutions of **1-(NCO)(μ_2-N^{13}CO)** to stand for extended periods showed no change as evidenced by ^{13}C NMR or infrared spectroscopy, indicating that although μ-nitrido



1-(NCO)(μ_2-NCO)　**1-(NCO)(μ_2-N^{13}CO)**

Scheme 3.

carbonylation is reversible, the two isocyanate ligands do not exchange at ambient temperature.

To determine if the coordination of DMAP to trap μ-nitrido hafnocene complexes following N_2 carbonylation was unique to **1-N$_2$** or a more general process, experiments with other activated hafnocenes were performed. Carbonylation of either the *ansa*-hafnocene dinitrogen compound, $[\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}t\mathrm{Bu})Hf\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$, or $[\{(\eta^5\text{-}C_5Me_4H)_2Hf\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ with 1–4 atm of CO in the presence of one equivalent of DMAP resulted in clean formation of the hafnium oxamidide compounds $[\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3\text{-}3\text{-}t\mathrm{Bu})Hf\}_2(N_2C_2O_2)]$ and $[\{(\eta^5\text{-}C_5Me_4H)_2Hf\}_2(N_2C_2O_2)]$, respectively. Analysis by ^{1}H and ^{13}C NMR spectroscopy provided no evidence for formation of other products or intermediates. These results suggest that less sterically demanding cyclopentadienyl ligands in **1-N$_2$** stabilize dimeric μ-nitrido intermediates likely due to the accessibility of the bimetallic species and ability to coordinate exogenous ligands such as substituted pyridines.

In summary, we report the first examples of isolated and structurally characterized hafnocene μ-nitrido complexes following CO-induced N_2 cleavage. These compounds are stabilized by coordination of 4-substituted pyridines and have been demonstrated to be viable intermediates in nitrido carbonylation to form a bridging hafnocene isocyanate derivative. Additional nitrogen functionalization reactivity with these compounds is currently under investigation.

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[16] CCDC 866377 (**1-N$_2$(DMAP)**) 866378 (**1-(N)(NCO)(4-OMe-Py)**), and 866379 (**1-(N)(NCO)(DMAP)**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.