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Nitrogen–Carbon Bond Formation from N_2 and CO_2 Promoted by a Hafnocene Dinitrogen Complex Yields a Substituted Hydrazine**

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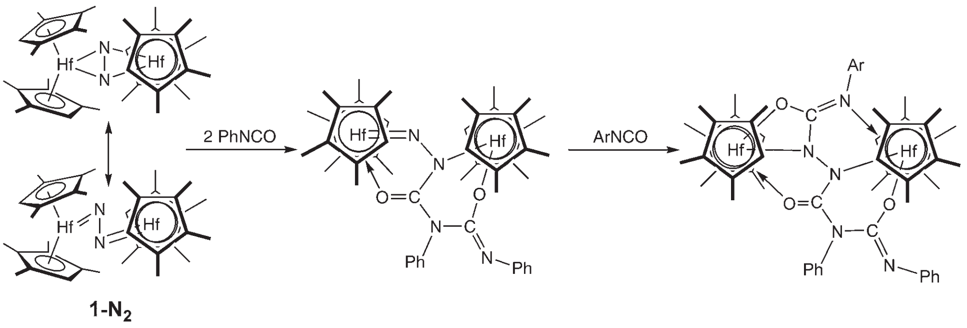
The discovery of methods for the assembly of nitrogen–carbon bonds from abundant chemical feedstocks is a continuing chemical challenge given the importance of amines and heterocycles in pharmaceutical, agrochemical, and electronic materials applications.[1] Synthetic ammonia currently serves as the primary nitrogen source for many of these compounds,[2] and efforts continue to expand its role in synthesis.[3] Because of the high energy demands associated with the Haber–Bosch process,[4] direct elaboration of typically inert atmospheric N_2 into more value-added organic molecules is attractive for the evolution of ammonia-independent synthetic pathways.[5]

Addition of nonpolar reagents such as dihydrogen,[6] terminal alkynes,[7] saturated carbon–hydrogen bonds,[8] and proton donors[7] to activated early-transition-metal dinitrogen compounds[9] has emerged as a powerful approach for the assembly of N–H bonds under mild conditions. For cyclopentadienyl-supported zirconium compounds, computational[10,11] and experimental[10] studies have established the importance of "imido character" in the metal–nitrogen bonds to facilitate the 1,2-addition of dihydrogen and C–H bonds.

Promoting nitrogen–carbon bond formation using cycloaddition pathways has proven more challenging. Fryzuk and co-worker's report of the addition of terminal alkynes to a side-on bound zirconium dinitrogen compound to form one new N–C bond[12] has demonstrated the validity of this approach. However in bis(cyclopentadienyl)zirconium chemistry, addition of internal alkynes or aryl isocyanates to $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ induced loss of dinitrogen.[8,13] Because deleterious side-on, end-on isomerization of the $[N_2]^{4-}$ ligand was believed to be the origin of this unwanted reactivity, the cycloaddition chemistry of the corresponding hafnocene complex, $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**1-N$_2$**), was explored. Treatment of **1-N$_2$** with two equivalents of PhNCO yielded a product with a new nitrogen–carbon bond where the nitrogen atom was derived from N_2. The remaining Hf=N linkage in the product is also susceptible to further functionalization as the cycloaddition of terminal alkynes and aryl isocyanates forms N–H and N–C bonds, respectively (Scheme 1).



Scheme 1. N–C bond formation by addition of phenylisocyanate to **1-N$_2$**.

On the basis of these initial observations, addition of various heterocumulenes to **1-N$_2$** seemed a viable strategy for the assembly of nitrogen–carbon bonds from coordinated N_2. An alternative bonding description of the four-electron-reduced dinitrogen ligand in **1-N$_2$** is a bis(amido) fragment coordinated to each hafnium center,[14] suggesting that insertion of carbon dioxide may be feasible.[15] Herein, we describe the formation of nitrogen–carbon bonds from coordinated dinitrogen and carbon dioxide[16] and subsequent removal of the functionalized nitrogen core to form a dicarboxylated silyl-substituted hydrazine.

Addition of two equivalents of carbon dioxide to a solution of **1-N$_2$** in [D$_6$]benzene or toluene followed by recrystallization from a toluene solution layered with pentane at −35 °C furnished a red solid identified as $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(NCO_2)_2$ (**1-N$_2$C$_2$O$_4$**), arising from formal insertion of two equivalents of CO_2 into the Hf–N bonds of one side of the $[N_2]^{4-}$ subunit (Scheme 2).

The ^{1}H NMR spectrum of **1-N$_2$C$_2$O$_4$** in [D$_6$]benzene solution exhibits the number of cyclopentadienyl resonances expected for a dimeric molecule with idealized C_2 symmetry. Treatment of the ^{15}N-labeled dinitrogen complex, **1-^{15}N$_2$**,[14] with $^{13}CO_2$ gave rise to a doublet centered at $\delta = 155.77$ ppm

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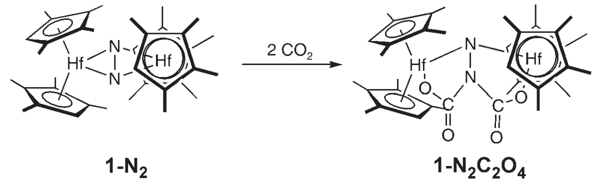


Scheme 2.

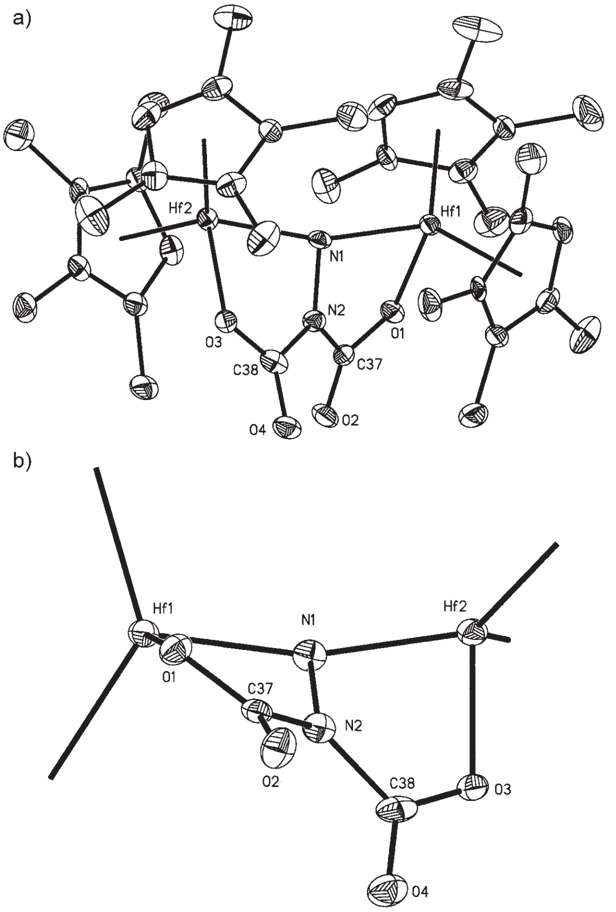


Figure 1. a) ORTEP drawing of the molecular structure of **1-N$_2$C$_2$O$_4$** with 30% probability ellipsoids. b) A view of the core of the molecule. Hydrogen atoms are omitted for clarity.

in the ^{13}C NMR spectrum, consistent with N−C bond formation from N$_2$ and CO$_2$. Additional support for this assignment of the solution structure was provided by ^{15}N NMR spectroscopy. Exposure of **1-^{15}N$_2$** to two equivalents of CO$_2$ (natural abundance) generated **1-^{15}N$_2$C$_2$O$_4$**, which exhibited two doublets ($^1J_{N,N}=13.1$ Hz) centered at $\delta=184.0$ and 319.6 ppm for the inequivalent nitrogen atoms. The solid-state (KBr) infrared spectrum of **1-N$_2$C$_2$O$_4$** contains two strong C=O bands centered at 1728 and 1662 cm^{-1} and a stretch at 1159 cm^{-1} assigned as a C−O band. All three bands shift appropriately (1687, 1625, and 1133 cm^{-1}, respectively) upon preparation of **1-N$_2$^{13}C$_2$O$_4$** from ^{13}CO$_2$.

The identity of **1-N$_2$C$_2$O$_4$** was also established by single-crystal X-ray diffraction (Figure 1). In the solid state, the two hafnocene subunits are canted with respect to each other, forming a wedge dihedral angle of 87.4°. This angle is defined by the planes formed from the cyclopentadienyl centroids and the hafnium atoms. The $[N_2C_2O_4]^{4-}$ core is comprised of two fused five-membered rings that are conjoined by the N1–N2 bond. For Hf1, the N1 and O1 atoms are contained in the metallocene wedge with the functionalized nitrogen atom N2 dipped below this plane. Accordingly, the wedge for Hf2 contains N1 and O3 with the C38 carboxylate fragment distorted from the wedge.

The N1–N2 bond length of 1.471(7) Å and C37–O1 and C38–O3 bond lengths of 1.323(7) and 1.303(8) Å, respectively, are consistent with single bonds. The contracted C37–O2 and C38–O4 bond lengths of 1.208(8) and 1.228(8) Å suggest localized C=O bonds. The Hf1–N1 and Hf2–N1 distances of 2.137(5) and 2.131(5) Å are as expected for hafnium amides.

Attempts were made to observe intermediates on the dinitrogen functionalization pathway by adding substoichiometric amounts of carbon dioxide. Treatment of **1-N$_2$** with one equivalent of CO$_2$ yielded two new organometallic products along with 30% of **1-N$_2$C$_2$O$_4$** and 40% of the starting dinitrogen compound. The first new product, accounting for approximately 15% of the mixture, was of C_{2v} molecular symmetry (**A**) and exhibited ^{13}C and ^{15}N NMR resonances centered at $\delta=165.9$ and 309 ppm, respectively, upon isotopic labeling. These resonances, in combination with a coupling constant ($^1J_{N,C}$) of 12.1 Hz, are consistent with N−C bond formation.

A second new organometallic product (**B**) was also formed in 15% yield and exhibited overall C_2 or C_s molecular symmetry as judged by ^{1}H NMR spectroscopy. A similar ^{13}C NMR shift of $\delta=167.3$ ppm and coupling constant $^1J_{C,N}=9.9$ Hz were observed upon isotopic labeling and are also consistent with N−C bond formation. Importantly, neither **A** nor **B** converts into **1-N$_2$C$_2$O$_4$** with addition of CO$_2$. Tentative structures based on spectroscopic and reactivity data and literature precedent[15] are presented in Figure 2. Unfortunately, definitive characterization of these compounds was hampered by their instability ($t_{1/2}=6$–10 h in [D$_6$]benzene) and difficulty in separating them from **1-N$_2$C$_2$O$_4$** and **1-N$_2$**. By way of comparison, the half-life for **1-N$_2$C$_2$O$_4$** is approximately 4 days in [D$_6$]benzene at 23 °C. Because both **A** and **B** only appear at lower carbon dioxide concentrations, they most likely arise from a unimolecular isomerization process that competes with insertion of a second equivalent of CO$_2$ during the formation of **1-N$_2$C$_2$O$_4$**. The analogous reaction, whereby the zirconium dinitrogen complex, $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$, was treated with two equivalents of CO$_2$ has also been conducted and yields a product distinct from those isolated from **1-N$_2$**. The chemistry of zirconium remains an active area of investigation.

With a hafnocene complex containing a functionalized dinitrogen fragment in hand, attempts were made to remove the $[N_2C_2O_4]^{4-}$ core as a stable organic molecule. Because **1-N$_2$C$_2$O$_4$** contains potentially robust hafnium–oxygen bonds, strong electrophiles were initially explored. Addition of excess Me$_3$SiI to solutions of **1-N$_2$C$_2$O$_4$** in [D$_6$]benzene or toluene produced an immediate change in color from orange

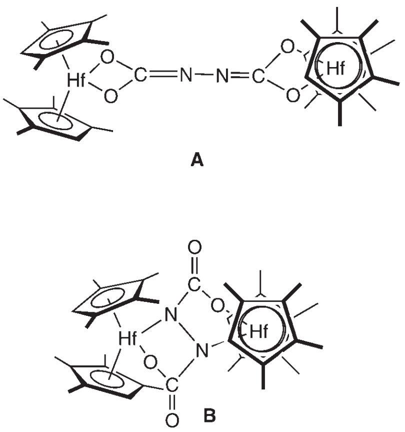
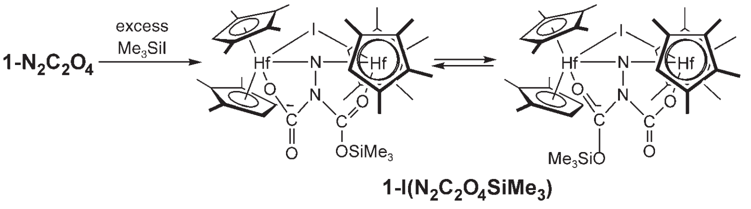


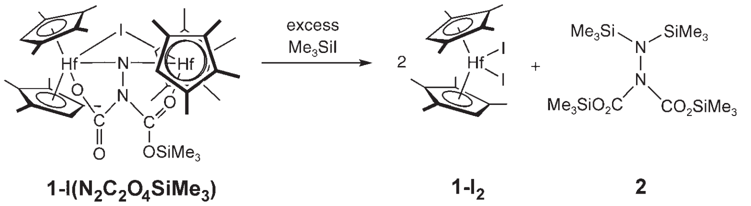
Figure 2. Proposed structures for **A** and **B** obtained from treatment of **1-N$_2$** with less than two equivalents of CO$_2$.

to pale yellow. The ^{1}H NMR spectrum of the kinetic product in [D$_6$]benzene exhibited C_s molecular symmetry with a new resonance for SiMe$_3$ centered at $\delta = 0.44$ ppm. Accordingly, a new ^{29}Si NMR peak was observed at $\delta = 24.41$ ppm. Based on these data and an X-ray diffraction study (see Supporting Information), the kinetic product of Me$_3$SiI addition was identified as the dihafnocene complex bearing a bridging iodide and a silylated carbonyl (Scheme 3). The higher symmetry observed by solution NMR spectroscopy suggests a rapid silicon migration between the carbonyl ligands.[17]

Further monitoring of the addition of Me$_3$SiI to **1-I(N$_2$C$_2$O$_4$SiMe$_3$)** by NMR spectroscopy established near-quantitative formation of (η^5-C$_5$Me$_4$H)$_2$HfI$_2$ along with a new organonitrogen species identified as the dicarboxyl silyl-substituted hydrazine, (Me$_3$Si)$_2$N-N(CO$_2$SiMe$_3$)$_2$ (**2**; Scheme 4). The ^{1}H NMR spectrum of **2** exhibits two singlets at $\delta = 0.24$ ppm and 0.39 ppm and the ^{29}Si NMR spectrum reveals resonances at $\delta = 6.16$ and 24.41 ppm. The ^{13}C-labeled isotopologue, prepared from **1-N$_2$^{13}C$_2$O$_4$**, exhibits a singlet at $\delta = 157.70$ ppm in the ^{13}C NMR spectrum. This peak splits into a doublet ($^1J_{C,N} = 20.6$ Hz) upon additional labeling with ^{15}N$_2$. In addition, GC-MS analyses of **2** prepared with both natural abundance and ^{13}C-labeled carbon dioxide produced molecular ions with m/z 408 and 410, respectively, further confirming its synthesis from N$_2$ and CO$_2$. The formation of (η^5-C$_5$Me$_4$H)$_2$HfI$_2$ with concomitant release of **2** offers the potential for recycling the hafnium[18,19] if more compatible routes for the synthesis of **1-N$_2$** are discovered. Note that optimal procedures for the separation of **2** from (η^5-C$_5$Me$_4$H)$_2$HfI$_2$ have not been developed.



Scheme 3.



Scheme 4.

In summary, functionalization of a side-on bound hafnocene dinitrogen complex with carbon dioxide has been accomplished. Both multinuclear NMR spectroscopy and X-ray diffraction studies established the identity of the product as arising from formal insertion of two equivalents of CO$_2$ into an [N$_2$]$^{4-}$ ligand with significant hafnium diamide character. Elaboration of the core of the molecule was accomplished by treatment with Me$_3$SiI, resulting in the synthesis of a dicarboxylated silylated hydrazine directly from N$_2$ and CO$_2$.

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