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N−C Bond Formation Promoted by a Hafnocene Dinitrogen Complex: Comparison of Zirconium and Hafnium Congeners

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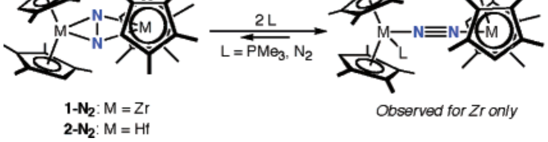
The discovery of activated, side-on bound zirconium dinitrogen complexes has broadened the scope of the known transformations involving coordinated N_2,[1] including the assembly of N−H bonds in solution from the corresponding elements.[2,3] Work in our laboratory with substituted bis(cyclopentadienyl) zirconium compounds has established the importance of twisted, dimeric, side-on N_2 complexes for imparting imido character in the Zr−N bonds, facilitating the 1,2-addition of H_2 and saturated hydrocarbons.[4,5] With this mechanistic foundation in hand, we have turned our attention to the synthesis of nitrogen−carbon bonds by a similar pathway. Here we describe the functionalization of coordinated N_2 by cycloaddition of phenyl isocyanate with a hafnocene dinitrogen complex and highlight important reactivity differences with its zirconocene congener.

By analogy to known chemistry of zirconocene imides,[6] the 1,2-addition of an unsaturated organic molecule to form nitrogen−carbon bonds would be a complementary synthetic method to Chatt-type functionalization procedures that rely on electrophilic addition or acylation of coordinated N_2.[7] Recently, Fryzuk and co-workers have provided precedent for this transformation with the cycloaddition of terminal alkynes with a side-on bound zirconium dinitrogen compound bearing a macrocyclic bis(phosphine)diamide ligand.[8] In contrast, addition of terminal alkynes to $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**1-N₂**) resulted in 1,2-addition of the C−H bond to yield the acetylide zirconocene diazenido compounds, $[(\eta^5\text{-}C_5Me_4H)_2Zr(C{\equiv}CR)]_2(\mu_2,\eta^2,\eta^2\text{-}N_2H_2)$.[9]

In an attempt to expand the scope of 1,2-addition to include nitrogen−carbon bond-forming reactions, **1-N₂** was treated with internal alkynes and heterocumulenes. Addition of 2-butyne to **1-N₂** resulted in the coupling of 2 equiv of alkyne to yield the corresponding zirconacycle[9] with N_2 loss. Likewise, treatment of **1-N₂** with a slight excess of PhNCO produced a complex mixture of products along with 87% of the gas expected for the loss of 1 equiv of free N_2 (Toepler pump).

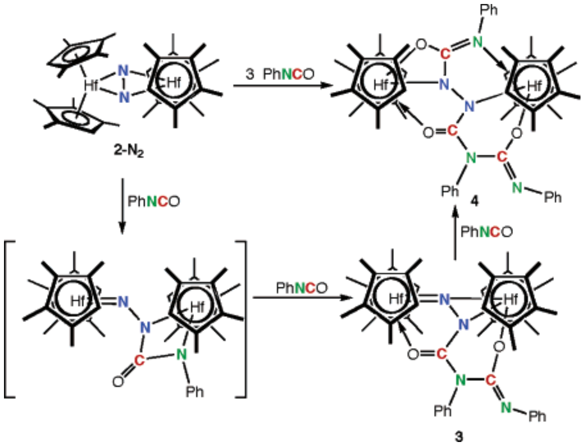
Suspecting that competitive ligand-induced side-on, end-on isomerization was the origin of N_2 dissociation, **1-N₂** was treated with σ-donors. Addition of 2 equiv of PMe_3 to **1-N₂** yielded $[(\eta^5\text{-}C_5Me_4H)_2Zr(PMe_3)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$ (**1-PMe₃**), similar to $[(\eta^5\text{-}C_5Me_4H)_2Zr(\eta^1\text{-}N_2)]_2(\mu_2,\eta^1,\eta^1\text{-}N_2)$, which is observed in small quantities under N_2 (eq 1).[4]



(1)

Exposure of **1-PMe₃** to 1 atm of H_2 furnished $(\eta^5\text{-}C_5Me_4H)_2ZrH_2(PMe_3)$, concomitant with N_2 loss, demonstrating the impact of coordination of an additional ligand on the reactivity of the N_2 ligand. Based on these observations, coordination of internal alkynes to the zirconium appears to induce more rapid side-on, end-on isomerization, reducing the activation of the N_2 ligand, resulting in dissociation rather than cycloaddition.

Scheme 1



To circumvent these complications, a more strongly activated side-on dinitrogen compound was targeted with the hypothesis that ligand-induced N_2 isomerization would be less competitive. Our laboratory has previously reported the synthesis and hydrogenation chemistry of the hafnium congener of **1-N₂**, $[(\eta^5\text{-}C_5Me_4H)_2Hf]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**2-N₂**).[10] In the solid state, **2-N₂** exhibits shorter metal−nitrogen bonds, an elongated N−N linkage, and a blue-shifted LMCT band relative to **1-N₂**, suggesting increased imido character in the M−N bonds. Exposure of **2-N₂** to 1 atm of dinitrogen or up to 10 equiv of PMe_3 produced no change in the ^1H NMR or toluene solution IR spectra, suggesting that the ligand-induced isomerization does not occur as readily as with **1-N₂**. However, preparation of **2-¹⁵N₂** by treatment of **2-N₂** with $^{15}N_2$ gas demonstrates such intermediates are kinetically accessible.

The reduced propensity of **2-N₂** to participate in ligand-induced isomerization prompted exploration of N_2 functionalization by cycloaddition. Addition of 2 equiv of phenyl isocyanate to **2-N₂** produced a new C_1 symmetric product, **3**, with retention of the N_2 core (Scheme 1). The solid-state structure of **3** (Figure 1a) establishes incorporation of 2 equiv of the isocyanate into the dinitrogen complex. In the $[N_4C_2O_2]^{4-}$ core, N(2) is 0.5917(16) Å deviated from the plane defined by Hf(2), N(1), and C(37) and is most likely formed from initial C═N cycloaddition to coordinated N_2, followed by C═O insertion into the newly formed hafnium−nitrogen bond.[11] The N(1)−N(2) bond elongates to 1.464(2) Å, while the Hf(1)−N(1) distance of 2.0635(16) Å is indicative of significant imido character.[12]

The ^1H NMR spectrum of **3** in toluene-d_8 at −80 °C exhibited the number of resonances expected for a C_1 symmetric molecule, in agreement with the solid-state structure. Warming the solution to 23 °C produced broadened peaks, consistent with a dynamic

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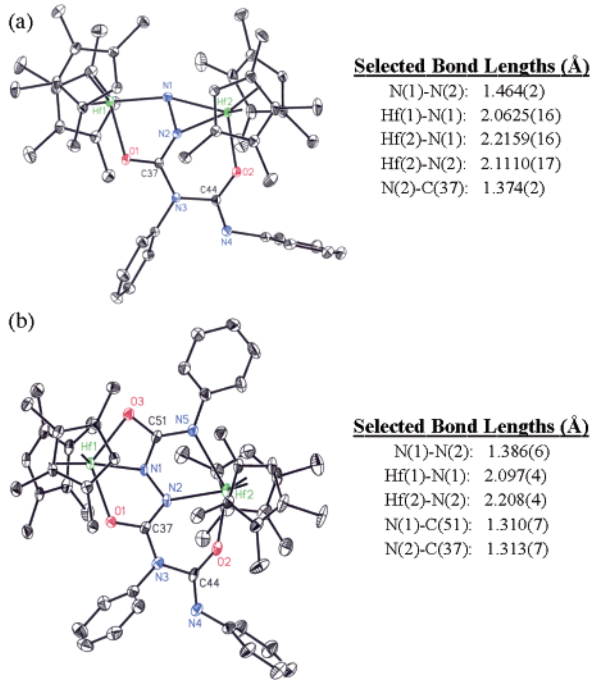


(a) **Selected Bond Lengths (Å)**

N(1)-N(2):	1.464(2)
Hf(1)-N(1):	2.0625(16)
Hf(2)-N(1):	2.2159(16)
Hf(2)-N(2):	2.1110(17)
N(2)-C(37):	1.374(2)

(b) **Selected Bond Lengths (Å)**

N(1)-N(2):	1.386(6)
Hf(1)-N(1):	2.097(4)
Hf(2)-N(2):	2.208(4)
N(1)-C(51):	1.310(7)
N(2)-C(37):	1.313(7)

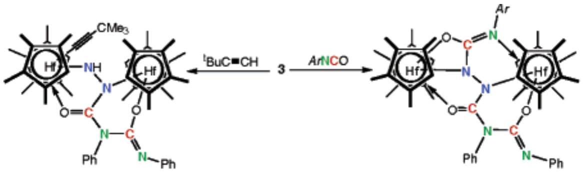
Figure 1. (a) Molecular structure of **3** and (b) **4** at 30% probability ellipsoids.

process, most likely inversion of the $[N_4C_2O_2]^{4-}$ core,[9] on the NMR time scale. The $\{^1H\}^{15}N$ NMR spectrum of isotopically labeled **3**, prepared from **2-^{15}N$_2$**, in benzene-d_6 at 23 °C displayed two broad signals centered at 423.7 (Hf = *N*(*1*)) and 181.5 (Hf-*N*(*2*)-C(37)) ppm.

Because the solid-state structure established significant hafnium imido character, additional Hf═N cycloadditions were explored. Treatment of **3** with additional PhNCO yielded **4**, arising from C═O cycloaddition to the Hf—N bond, to form a second N—C linkage from coordinated N_2. The solid-state structure of **4** (Figure 1b) confirms the new Hf—N—C—O metallacycle and establishes an overall coordination environment similar to **3**. Curiously, the N—N bond contracts to 1.386(6) Å, while the Hf(1)—N(1) distance is virtually unchanged at 2.097(4) Å. The newly formed N(1)—C(51) bond has a distance of 1.310(7), suggestive of imine character.

A similar product, **5**, was isolated from addition of 1 equiv of *p*-tolyl isocyanate to **3** (eq 2). The reversibility of isocyanate cycloaddition was probed with a crossover experiment. Heating a benzene-d_6 solution of **4** and excess *p*-tolyl isocyanate to 95 °C for 24 h produced no change, demonstrating that the final cycloaddition is irreversible under these conditions.

The hafnium imido character of **3** was also demonstrated by the 1,2-addition of a C—H bond of a terminal alkyne. Addition of 1 equiv of *t*-BuC≡CH yielded the product of C—H activation, **6**, forming a hafnium acetylide and an N—H bond (eq 2). Compound **6** was identified by characteristic N—H and C≡C infrared stretches centered at 3290 and 2200 cm^{-1}, respectively. The benzene-d_6 ^1H—^{15}N HSQC NMR spectrum demonstrated a correlation between the N—H resonance at 2.43 ppm and a doublet centered at 194.8 ppm in the ^{15}N NMR spectrum. Further support for this assignment was provided by the absence of the peak at 2.43 ppm when **3** was treated with *t*-BuC≡CD. The presence of a N—D bond was confirmed by ^2H NMR spectroscopy.



(2)

6

5: *Ar* = *p*-Me-C_6H_4

In summary, we have demonstrated that the hafnocene dinitrogen complex, **2-N$_2$**, is less prone to undergo deleterious ligand-induced N_2 isomerization, resulting in N_2 dissociation. The stabilization of the side-on dinitrogen complex permits elaboration of the imido-like Hf—N bonds, resulting in nitrogen—carbon bond formation upon addition of aryl isocyanates. Additional dinitrogen functionalization reactions that exploit these unique characteristics are under investigation in our laboratory.

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Supporting Information Available: Experimental procedures and crystallographic data for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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