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N_2 Activation by a Hafnium Complex: A DFT Study on CO-Assisted Dinitrogen Cleavage and Functionalization

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Dedicated, with admiration and in friendship, to Professor Gerhard Ertl

Since 1913, the Haber–Bosch process, in which N_2 is transformed into ammonia by catalytic hydrogenation, serves as the most important industrial nitrogen source for all human beings.[1] However, the unfavorable temperature and pressure conditions associated with the reaction cause high energy consumption. Therefore, seeking for an alternative way to activate and functionalize N_2 under ambient conditions remains a challenging and fascinating task for scientists.[2] In the last decade, numerous promising reactions approaching this long-standing goal have been discovered.[3] Among these studies, Chirik and co-workers reported the hydrogenation of N_2 via a dinuclear zirconium complex $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ at a temperature regime of 45–85 °C.[3d] It is intriguing that the analogous Cp* complex (Cp* = C_5Me_5) is incapable of undergoing N_2 hydrogenation.[4] Clearly, a seemingly trivial modification in the ligand sphere causes a remarkably different reactivity. Cyclopentadienyl-substituent effects[5] of this kind encouraged further exploration in the field of N_2 activation by Group 4 metallocenes. In fact, mechanistic studies soon followed[6] and more examples of N_2 hydrogenation were reported.[7] Besides H_2, these side-on metallocene dinitrogen complexes react with different organic substrates, for example, PhNCO[8] and CO_2,[9] allowing direct C–N bond formation without going through ammonia. However, in all these reactions the N–N bond of N_2 was never broken completely. Only very recently, Chirik and co-workers achieved complete N–N bond scission under mild conditions by adding CO to the N_2-bound hafnium complex **1**.[10] As shown in Scheme 1, complex **1** is transformed into different complexes, **2** or **3**, depending on the amount of CO; finally N-containing organic compounds are liberated by the addition of HCl. This is an exciting discovery on the grounds that i) it provides a new way to synthesize useful chemicals directly from inert N_2 and CO, and ii) with regard to the mechanism it involves several key steps like C–N bond coupling,[11] N–N bond cleavage,[12] and C–H bond activation.[13]

Quite clearly, a better understanding of the suggested mechanism underlying the reactions depicted in Scheme 1 is required. In view of the lack of any mechanistic or computational studies, we have performed density functional theory (DFT) calculations to explore plausible pathways for the proposed reactions shown in Scheme 1. We focused on the following critical features: i) how is the C–N bond formed, ii) what is the driving force for N–N bond cleavage, and iii) what promotes C–H bond activation?

In Figure 1, the pathways for the formations of **2** and **3** are presented together with the energetic profile and selected geometries (geometries of all species are shown in the Supporting Information). Optimized structures of **1**, **2**, and **3** are in good agreement with the reported crystal structures, validating the reliability of the B3LYP functional[14] and the basis sets employed in this study. The reaction starts with coordination of CO to the side-on N_2 hafnium complex **1**. This process has a barrier of 8.4 kcal mol^{-1} due to the bulky cyclopentadienyl ligand. The endothermicity of adduct formation reveals a rather weak Hf–CO interaction. However, the CO entity is capable of undergoing migratory insertion[15] into the Hf–N bond to give **5**. At high CO pressure, a second CO molecule may subsequently bind to the other Hf center of **5** and inserts into the Hf–N bond of **6** (red line in Figure 1), thus yielding the C_2-symmetric intermediate **7**. The activation and reaction energies for these two steps are comparable with those for the first CO, reflecting the symmetrical environment of the two Hf centers. Homolytic N–N bond cleavage takes place via **TS7/8**. In this step both Hf^{IV} centers are reduced to Hf^{III} and two isocyanate ligands are formed simultaneously. An intrinsic reaction coordinate

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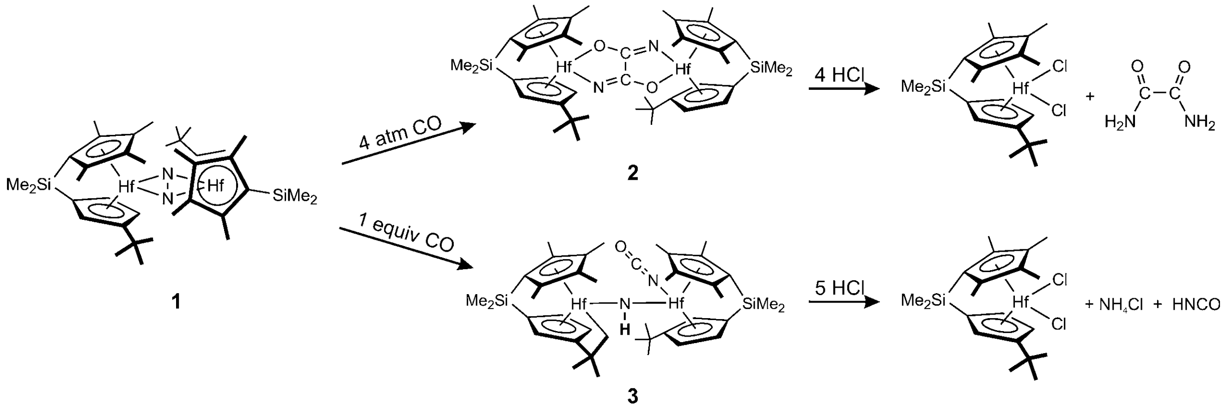


Scheme 1.

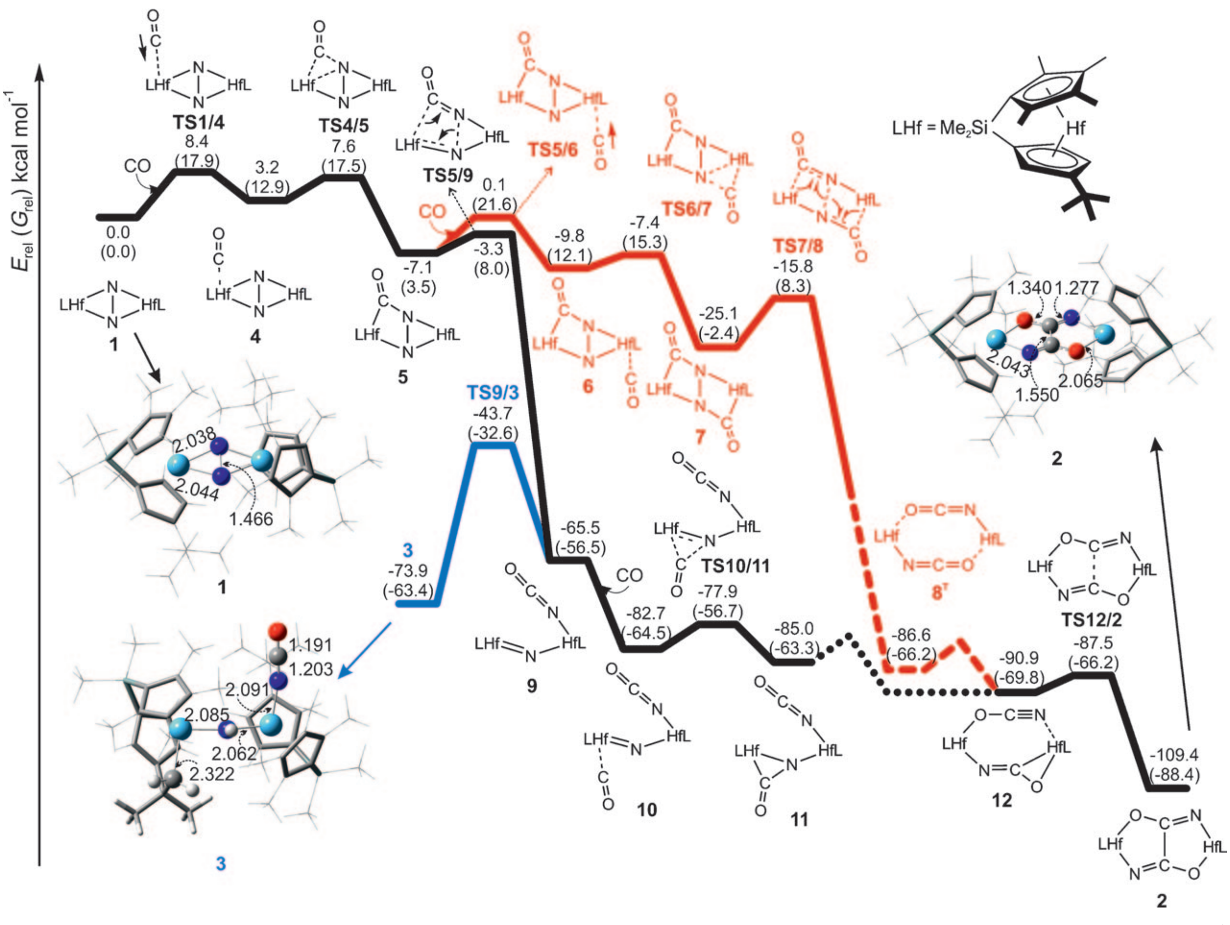


Figure 1. Potential-energy surfaces of the proposed pathways for the formations of **2** and **3**, and optimized geometries of **1**, **2**, and **3** (distances in Å). The relative electronic energies and Gibbs free energies (in parentheses) are given in kcal mol^{-1}.

(IRC) calculation[16] on **TS7/8** results in **7** for the reverse direction but does not converge for the forward direction on the singlet surface; however, an optimization of a forward point on the triplet surface leads to $\mathbf{8}^\mathbf{T}$, which is the only species with a triplet ground state in Figure 1.[17] Given the C_2 symmetry of both **7** and **TS7/8** and the extreme exothermicity, it is reasonable to obtain $\mathbf{8}^\mathbf{T}$ as an intermediate. Species $\mathbf{8}^\mathbf{T}$ might then convert to the slightly more stable singlet **12** in a two-state-reactivity scenario that is believed to prevail for the third-row transition-metal complexes.[18] Next, **12** undergoes C–C bond coupling via **TS12/2** to yield product **2**. An analogous coupling process for CO_2, which is isoelectronic to OCN^- was reported recently,[19] and the details of the C–C bond coupling in yet another carbonylation reaction were analyzed quite some time ago.[20]

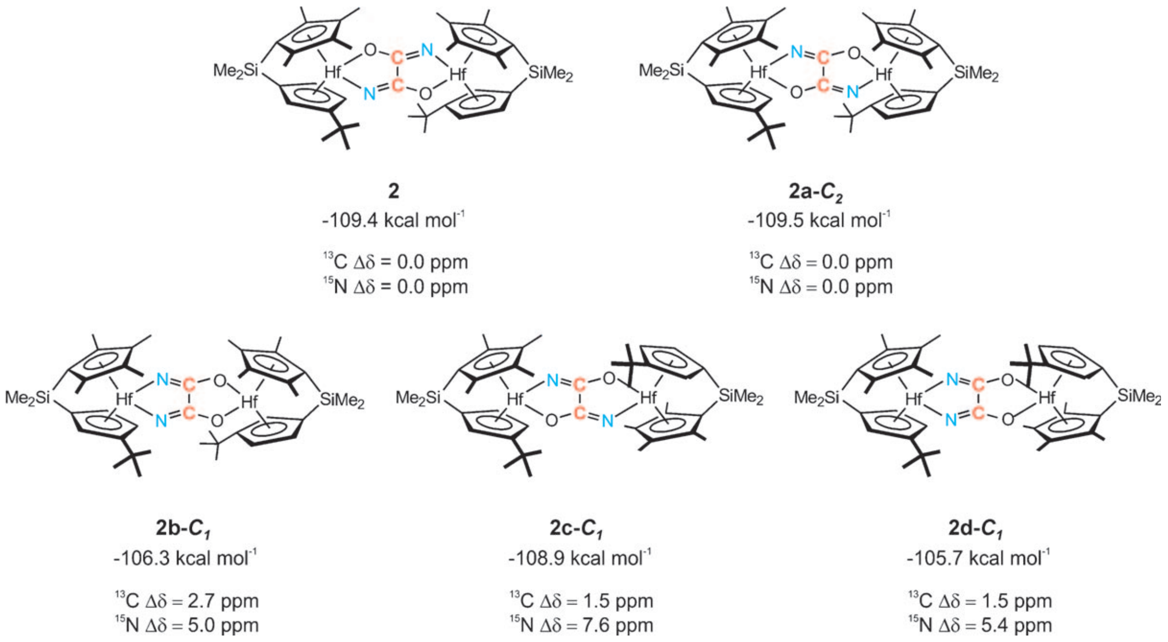
We have also considered some mechanistic alternatives. Species **5** may undergo a retro[2+2] cycloaddition via **TS5/9** without adding a second CO molecule. This results in the splitting of the N–N bond with an even lower barrier of 3.8 kcal mol^{-1} (compared with **TS7/8**) and gives **9** as an intermediate that possesses an imido and an isocyanate ligand. The large exothermicity of this step ensures irreversibility. If no extra CO is present (1 equiv CO), intramolecular addition of a C–H bond of the *tert*-butyl substituent to the Hf=N bond (**TS9/3**) generates the experimentally observed product **3** (blue line in Figure 1, details see below). Otherwise, if CO pressure permits, a second CO molecule can barrierlessly bind to the vacant coordination site of **9** to form **10**, and then migratory insertion into the Hf=N bond gives rise to **11** with an associated barrier of only 4.8 kcal mol^{-1}. Numerous isomers of **11** with different binding modes between the two OCN$^-$ ligands and the two Hf centers do exist, and they are not too different energetically. Although these isomers may be related to the unidentified C_1-symmetric product(s) in the experiment, we do not intend to discuss the structural and energetic details of these isomers since these aspects do not form the main subject of this Communication. We assume that **11** undergoes a series of isomerizations to form **12** and eventually the final product **2**.

In addition to the electronic energies, in Figure 1 also the Gibbs free energy values are given. The corresponding potential energy surfaces are rather similar concerning intramolecular transformations, but differ for those steps in which a CO molecule is added because of the entropic contribution. However, using G_{rel} does not affect our main conclusions which are based on the electronic energies. We have also performed calculations using the polarizable continuum model (PCM) to estimate solvent effects.[21] The energy differences in the gas phase and with toluene as a solvent for the crucial species **1**, **2**, **3**, **5**, **9**, **TS5/9**, and **TS9/3** are 0.0, 0.0, 1.0, −1.3, −2.6, −0.6, and 0.6 kcal mol^{-1}, respectively. As the differences are quite small, the solvent effects have not been taken into account in our discussion.

The theoretical attempt to indentify the suggested but experimentally unidentified C_1-symmetric product(s),[10] was so far unsuccessful. The calculated relative energy and the $\Delta\delta$ values of possible isomers of **2** are presented in Figure 2. Since all isomers are rather similar in energy, none of them can be excluded rigorously. A comparison of the experimental NMR $\Delta\delta$ values (^{13}C: 1.5 ppm; ^{15}N: 0.9 ppm) and the computed ones shows that none of the proposed C_1 structures is preferred because the chemical environments of the two nitrogen atoms in the C_1 structures are quite different. Therefore, the identity of the preferred isomer cannot be derived from the present DFT calculations.

As discussed above, due to the complexity of the system, one should of course be cautious to exclude rigorously other reaction pathways. Yet, the potential-energy surface (PES) in Figure 1 provides us with some hints to answer the three questions raised above. For instance, the barriers for the C–N bond formation steps (**TS4/5**, **TS6/7**, and **TS10/11**) are lower than 10 kcal mol^{-1}, and can thus be easily overcome at room temperature.

Another obvious piece of information from Figure 1 is the large downhill reaction energy associated with the N–N bond cleavage. This implies that the N–N bond scission (via **TS5/9** or **TS7/8**) is irreversible. In general, it is usually proposed that N_2 cleavage takes place at low-valent metal (Mo^{III},[3a,22] Nb^{IV},[12c,23] and Ta^{III}[3f,24]) complexes in which the



2
-109.4 kcal mol^{-1}
^{13}C $\Delta\delta$ = 0.0 ppm
^{15}N $\Delta\delta$ = 0.0 ppm

2a-C_2
-109.5 kcal mol^{-1}
^{13}C $\Delta\delta$ = 0.0 ppm
^{15}N $\Delta\delta$ = 0.0 ppm

2b-C_1
-106.3 kcal mol^{-1}
^{13}C $\Delta\delta$ = 2.7 ppm
^{15}N $\Delta\delta$ = 5.0 ppm

2c-C_1
-108.9 kcal mol^{-1}
^{13}C $\Delta\delta$ = 1.5 ppm
^{15}N $\Delta\delta$ = 7.6 ppm

2d-C_1
-105.7 kcal mol^{-1}
^{13}C $\Delta\delta$ = 1.5 ppm
^{15}N $\Delta\delta$ = 5.4 ppm

Figure 2. Possible isomers of **2**. $\Delta\delta$ refers to the difference of ^{13}C (^{15}N) chemical shift of two C (N) atoms highlighted in red (blue). The relative electronic energies are given in kcal mol^{-1}.

metal stores enough electrons to break the N−N bond. What about the high-valent Chirik Hf^{IV} complex? To understand the driving force for N−N bond cleavage, the N−N bond lengths of the relevant species along the reaction pathways are plotted in Figure 3. Once the hafnocene–N_2 complex **1** is formed, the triple bond of the dinitrogen molecule is elongated from 1.105 Å to 1.466 Å, which corresponds to a normal N−N single bond (1.47 Å).[25] The association of CO to **1** does not affect the N−N bond much until **5** is formed. An examination of the structure of **5** revealed several interesting factors which account for the large driving force for the N−N bond cleavage. First, the small ∢HfCN angle of 87.1° for the sp^2-hybridized carbon reflects that the four-membered Hf-C-N-N ring is highly strained. As a result, the N−N bond is significantly weakened. Second, the compact environment causes a strong steric repulsion.[26] These two tensions are released dramatically by breaking the N−N bond. Similar arguments also apply for the homolytic N−N bond dissociation in **7**. Owing to the absence of a such strained four-membered ring, no N−N bond cleavage was observed in the reaction between metallocene–dinitrogen complexes with PhNCO[8] or CO_2.[9]

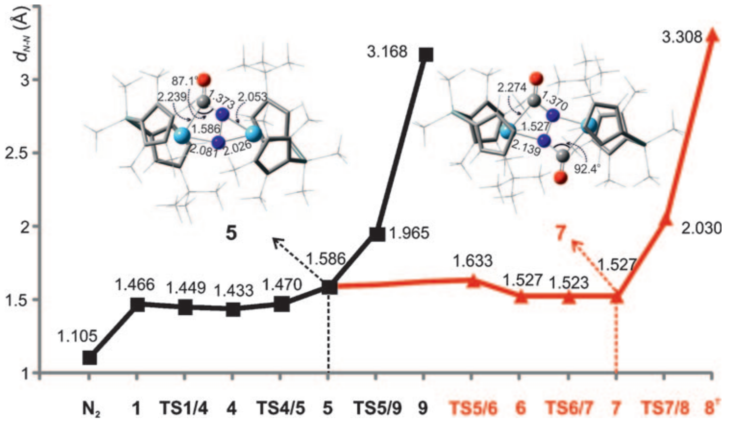


Figure 3. The calculated N−N bond lengths of relevant species along pathways and the optimized structures of **5** and **7** (distances and angles are in Å and degree respectively).

It is well known that metal–nitrogen multiple bonds promote C−H bond activation.[27] **1**, as a Group 4 metallocene–dinitrogen complex, was proposed to have partial "imido character",[6a,9a] while intermediate **9** is apparently a hafnium–imido complex. It is of interest to find out which of them facilitates the intramolecular C−H bond activation of the *tert*-butyl substituent of the cyclopentadienyl ring. The energy profiles for the 1,2-addition of the C−H bond to the Hf−N bond of **1** and **9** are presented in Figure 4 (blue line). The barrier of 39.4 kcal mol^{-1} for the direct addition of the C−H bond to the initial complex **1** is too high to be accomplished at room temperature. Thus, this endothermic step is unlikely to take place. The barrier for the 1,2-addition of the same C−H bond to the Hf=N bond in **9** is dramatically reduced to 21.8 kcal mol^{-1} and the reaction becomes exothermic. The Hf=N bond length (1.952 Å) of **TS9/3** is much shorter than the Hf−N bond length (2.232 Å) of **TS1/13**, indicating that the former is an imido and the latter an amido

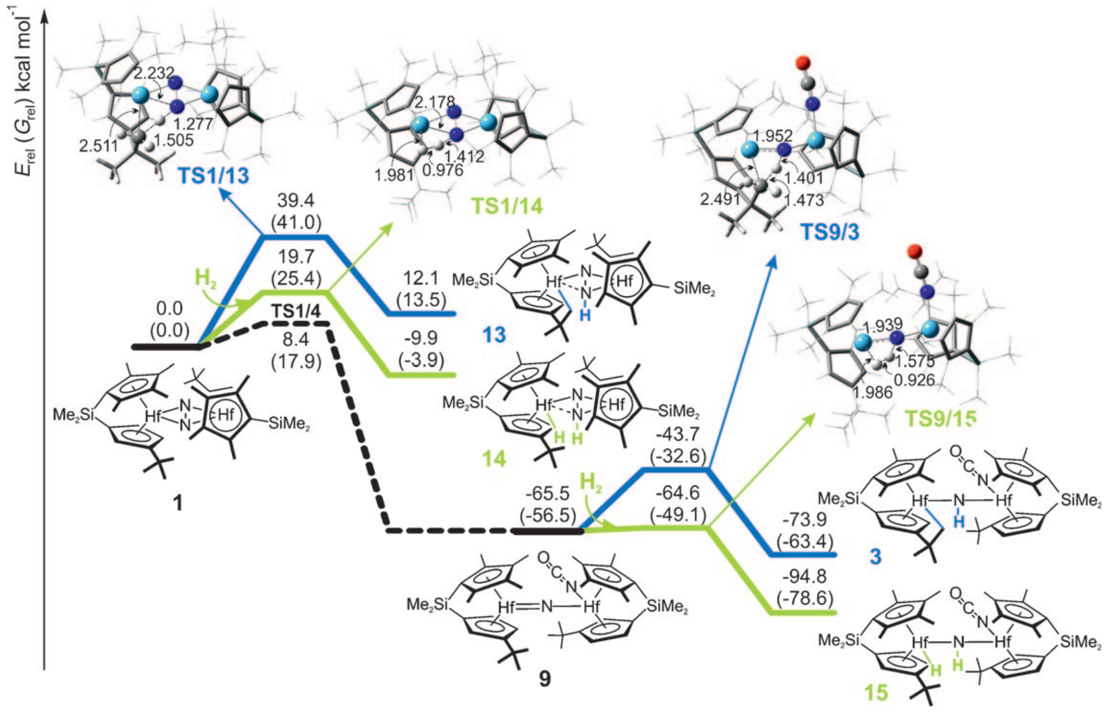


Figure 4. Energy profiles for the C−H bond activation (blue line) and the H−H bond activation (green line) by **1** and **9**, and the optimized transition structures (distances in Å). The relative electronic energies and Gibbs free energies (in parentheses) are given in kcal mol^{-1}.

bond. Clearly, the intramolecular C–H bond activation is promoted by the addition of CO to **1**. To find out whether this effect also exists in other systems, we calculated the intermolecular H–H bond addition to **1** and **9** (green line in Figure 4). The activation energy (19.7 kcal mol^{-1}) as well as the reaction energy (−9.9 kcal mol^{-1}) for the direct addition of H_2 to the Hf–N bond of **1** are comparable with those in previous computational studies on N_2 hydrogenation.[6b,d,17b] Again, the barrier for the addition of H_2 to the imido complex **9** is lowered to 0.9 kcal mol^{-1}, and therefore, almost negligible. Thus, our computational findings suggest that one should perform a reaction of **1** with a mixture of CO and H_2 as a decisive experiment to test the proposed reaction mechanism. In the presence of both H_2 and CO, due to the low barrier, complex **1** would react with CO first to give imido complex **9**, which could be trapped by H_2 to form **15**. If product **15** was obtained experimentally, it confirms the existence of transient **9** and, thus, the proposed mechanism. Moreover, the calculations also show the possibility of a cooperative activation of N_2. Addition of one equivalent of CO as an initiator might promote other functionalization reactions of N_2 via such side-on bound metallocene–dinitrogen complexes.[28]

In summary, the detailed mechanism for N_2 activation with CO promoted by a hafnocene complex was studied by DFT calculations. The computational results support and extend the mechanism proposed by Chirik and co-workers[10] and settle three critical issues: i) coordination and migratory insertion of CO into the Hf–N bond occur with very low barriers to form a C–N bond, ii) the ring strain in the four-membered Hf-C-N-N ring in **5** or **7** provides the driving force for the splitting of the N–N bond, iii) the transient intermediate **9** is an imido complex, which facilitates the 1,2-addition of a C–H or a H–H bond to the Hf–N bond.

Computational Section

The DFT calculations were performed with the Gaussian 09 package.[29] All energies presented were calculated at B3LYP/**BSII**//B3LYP/**BSI**. Geometries were optimized with basis sets **BSI** (LANL2DZ + f with ECP for Hf, 6-31 g(d) for others).[30] Frequency calculations at the same level of theory have been carried out to identify all stationary points and provide zero-point energy (ZPE) corrections. Single-point energies for all the structures were calculated with larger basis sets **BSII** (def2-TZVP with ECP for Hf, 6-311+G(2df) for N, and 6-311G(d) for others).[31] No significant energetic differences were found with different basis sets. Both singlet and triplet states have been considered and the former is calculated to be the ground state for most of the species. Solvent effects were estimated by single-point calculations at **B3LYP/BSII** using the polarizable continuum model (PCM). All relative energies (corrected for ZPE contributions) and Gibbs free energies (at 298 K) are reported in kcal mol^{-1}.

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Keywords: CO activation · C–H activation · C–N coupling · density functional calculations · nitrogen fixation

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[28] Note added in proof (16.09.2010): After submission of this manuscript, Chirik and co-workers reported the reaction of **1** with a mixture of CO and H_2. Their independent experimental findings confirm the formation of **15** predicted by us. Moreover the idea of using CO as an initiator to promote other functionalization reactions of N_2 has also been realized by the same group: D. J. Knobloch, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 10553–10564.

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