

On the Origin of Dinitrogen Hydrogenation Promoted by $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$

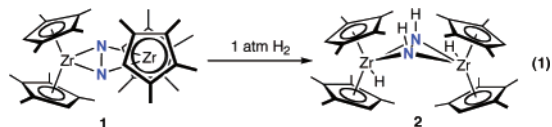
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The hydrogenation of molecular nitrogen to ammonia is one of the most important technological achievements of the past century, with annual production exceeding over 100 million tons.¹ Notably, synthetic ammonia is responsible for sustaining approximately 40% of the world's population and serving as the source of 40–60% of the nitrogen in the human body.¹ Despite the indispensability of this process, direct observation of the addition of H₂ to N₂ by a homogeneous metal complex in solution has been limited to only two examples.² Fryzuk has reported a dinuclear zirconium amido-phosphine ligated dinitrogen complex that reacts slowly with dihydrogen over the course of one week to afford one N–H bond and a bridging zirconium hydride.³ Computational studies have indicated that further hydrogenation of the N₂ ligand is thermodynamically feasible but is not observed experimentally due to a high kinetic barrier.⁴

Our laboratory has recently described the synthesis of the side-on bound zirconocene dinitrogen complex, $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$ (**1**).⁵ At ambient temperature, **1** reacts rapidly with 1 atm of dihydrogen to afford the zirconocene hydrazido complex, $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{ZrH}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2\text{H}_2)$ (**2**) (eq 1). Thermolysis at 85 °C under a dihydrogen atmosphere liberates small quantities of free ammonia.⁵ These observations contrast both the structure and reactivity of the related dinitrogen complex, $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\eta^1\text{-N}_2)]_2(\mu_2, \eta^1, \eta^1\text{-N}_2)$, a molecule that readily loses dinitrogen and forms $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ upon exposure to H₂.⁶ The latter behavior is typical of most metal dinitrogen compounds.⁷ Here we describe a combined computational and experimental study aimed at understanding the unprecedented reactivity of **1** with H₂.



Because the structure and reactivity of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\eta^1\text{-N}_2)]_2(\mu_2, \eta^1, \eta^1\text{-N}_2)$ and **1** are so vastly different, we explored the reduction of the “mixed ring” zirconocene complex, $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{-ZrI}_2$ (**3**).⁸ Stirring a toluene slurry of **3** with KC₈, followed by filtration and recrystallization, afforded a deep purple solid identified as $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Zr}(\eta^1\text{-N}_2)]_2(\mu_2, \eta^1, \eta^1\text{-N}_2)$ (**4**) on the basis of NMR and IR spectroscopy and Toepler pump experiments.⁹ Exposure of **4** to 1 atm of dihydrogen resulted in liberation of dinitrogen and yielded the zirconocene dihydride, $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{ZrH}_2$ (**5**) (eq 2).⁸ Thus, the steric protection provided by the ancillary ligand framework in **4** prevents formation of the electronically preferred side-on coordination of the N₂ ligand, which is essential for hydrogenation activity.

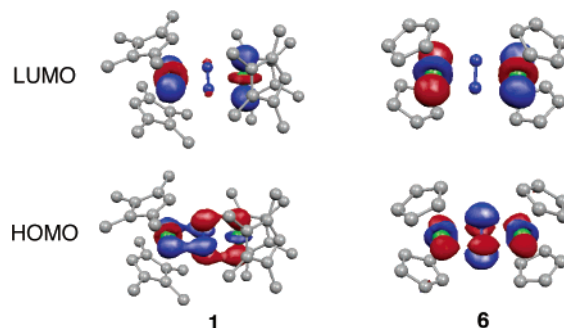
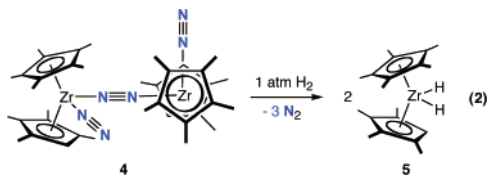


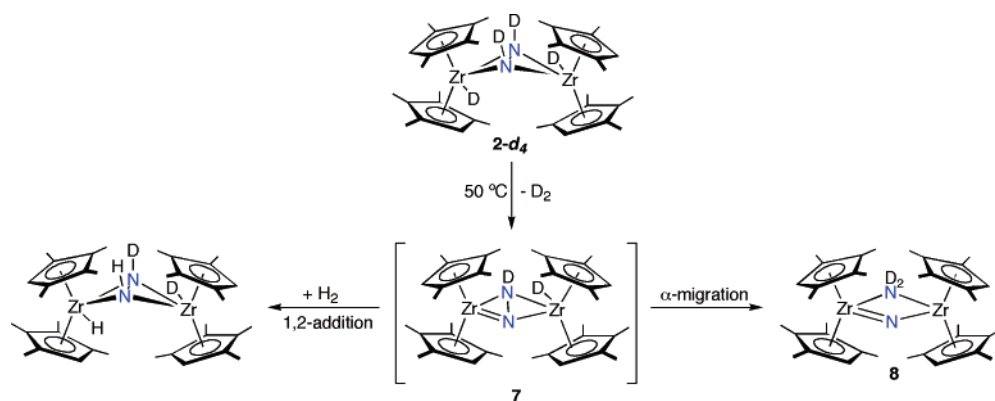
Figure 1. Frontier molecular orbitals of **1** and **6**.

Side-on coordination does not appear to be the only requirement for N₂ hydrogenation. Examples of side-on dinitrogen compounds that liberate N₂ upon addition of dihydrogen are known.^{7,10} Clearly other features of **1** contribute to its unique reactivity. The electronic structure of **1** was examined by density functional theory as implemented by the ADF program suite.⁹ The results from the calculation were in excellent agreement with the experimentally determined geometry. The frontier molecular orbitals of the optimized structure are shown in Figure 1, and a more complete diagram is presented in the Supporting Information. The LUMO of **1** is an in-phase linear combination of two zirconocene *Ia*₁ orbitals¹¹ which is well-suited to accommodate incoming H₂ molecules. Remarkably, the HOMO is the corresponding out-of-phase linear combination of zirconocene *Ia*₁ orbitals engaged in π -bonding with a π^* orbital of the N₂ ligand. This interaction is reminiscent of group 4 transition metal imido complexes¹² and suggests significant Zr=N character.^{13,14}

Computational studies were also performed on the hypothetical model complex, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$ (**6**), where the dihedral angle between the metallocene wedges was confined to 0°. The LUMO (Figure 1) is also comprised of zirconocene *Ia*₁ orbitals but unlike **1** is the out-of-phase linear combination. The in-phase combination comprises the HOMO and does not have the appropriate symmetry to engage in significant back-bonding with the N₂ ligand. The computational results clearly demonstrate the importance of the canted metallocene wedges (dihedral angle = 65.3°) in **1** for the hydrogenation of dinitrogen. This “twisted” ground-state structure allows opposite phase *Ia*₁ zirconocene orbitals to overlap with the orthogonal lobes of the N₂ π^* molecular orbital, imparting significant imido character into the Zr–N bonds and thereby enabling 1,2-addition of H₂.¹⁵

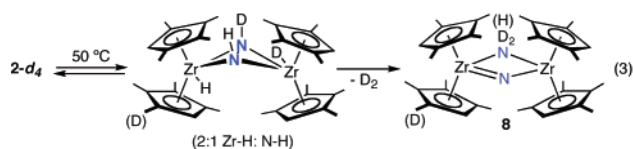
The 1,2-addition hypothesis was tested experimentally by a series of isotopic labeling experiments. Exposure of a benzene-*d*₆ solution of **2-d**₄⁵ to 4 atm of dihydrogen at 22 °C produced no isotopic exchange, demonstrating that the terminal zirconium hydrides do not readily participate in σ -bond metathesis. However, gently warming the sample to 50 °C produced Zr–H and N–H resonances in a 1:1 ratio as judged by ¹H NMR spectroscopy. Approximately 50% isotopic exchange occurred over the course of 24 h. These

Scheme 1



results are consistent with initial, rate-determining 1,2-elimination of D_2 to form intermediate **7**, which then captures free dihydrogen to afford the observed product (Scheme 1). Under conditions where **7** cannot be captured by free H_2 or D_2 , α -migration occurs, yielding the zirconocene μ -nitrido amido complex, **8** (Scheme 1). Significantly, hydrogenation of **8** is slow, requiring days at ambient temperature under 4 atm of H_2 to regenerate **2**.

The conversion of **2-d₄** to **8** was monitored by a combination of 1H and 2H NMR spectroscopy. Isotopic exchange is observed in the zirconocene hydrazido complex *before* conversion to **8**. A 2:1 ratio of Zr–H to N–H was measured, along with incorporation of deuterium into the cyclopentadienyl methyl groups (eq 3). Concomitant with the isotopic exchange observed for **2-d₄** is the observation of N–H bonds in **8** along with deuterium into the cyclopentadienyl ligands (eq 3).



The observed products are readily accommodated by a series of sequential 1,2-elimination and addition reactions. A detailed mechanistic scheme is presented in the Supporting Information. In the absence of H_2 (or D_2), intermediate **7** promotes the 1,2-addition of a cyclopentadienyl methyl group, which then, after side-on:endo-interconversion of the N(D)–N(H) unit, can undergo 1,2-elimination to complete the isotopic labeling of the C_5Me_4H ligand. Based on previous studies with $(\eta^5-C_5Me_4H)_2ZrH_2$,⁸ cyclometalation of the 1,4-methyl groups should be favored, although the poor resolution of the 2H NMR spectra makes a definitive assignment difficult. The observed preference for isotopic exchange into the Zr–D position over the N–D bond is rationalized on thermodynamic grounds on the known zero point energy differences between the two positions.¹⁶ However, it should be noted that the observed product ratios have not been shown to be at equilibrium and may be the result of numerous kinetic and equilibrium isotope effects.^{17,18}

In summary, we have provided both computational and experimental evidence for the importance of 1,2-addition in the hydrogenation of coordinated dinitrogen. “Imido-like” reactivity may be imparted to side-on bound zirconocene dinitrogen complexes where the planes of the metallocene wedges are significantly canted such that overlap with both N_2 π^* molecular orbitals may be achieved from opposite zirconium centers. Application of this mechanistic insight to new reactions for the functionalization of N_2 is currently under investigation in our laboratory.

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Supporting Information Available: Experimental and computational details and mechanistic scheme for isotopic exchange. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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