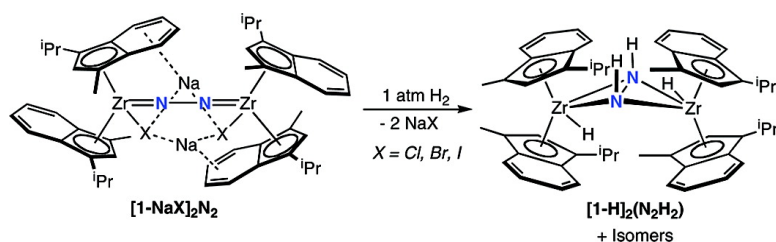Communication

N Hydrogenation from Activated End-On Bis(indenyl) Zirconium Dinitrogen Complexes

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N₂ Hydrogenation from Activated End-On Bis(indenyl) Zirconium Dinitrogen Complexes

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The synthesis of N−H bonds from molecular hydrogen and atmospheric nitrogen (N₂) is a challenge that has confronted chemists for the past century.[1] The Haber−Bosch ammonia synthesis has revolutionized global food production,[2] and the mechanism of the industrially implemented Fe−Ru catalysts has been the subject of intense investigation.[3] In contrast, the hydrogenation of coordinated N₂ with soluble transition metal complexes has only been known for a little over a decade.[4,5] This chemistry is dominated by "side-on" bound Zr and Hf complexes where the μ_2, η^2, η^2-N₂ hapticity serves to exclude additional π-acid coordination, increase metal−ligand backdonation, and generate strongly activated [N₂]⁴⁻ ligands. Subsequent computational investigations have posited that μ_2, η^2, η^2-N₂ (side-on) coordination is a "necessary condition" for successful dinitrogen hydrogenation[6] despite the well-established precedent for 1,2-addition to terminal group 4 imido compounds.[7] Here, we report the synthesis and characterization of bis(indenyl)zirconium dinitrogen compounds with strongly activated μ_2, η^1, η^1 N₂ (end-on) ligands that are readily hydrogenated.

Our laboratory has been exploring the chemistry of reduced indenyl zirconium derivatives.[8] For compounds bearing relatively large 1,3-ring substituents (e.g., SiMe₃ or ⁱPr), monomeric bis(indenyl)zirconium sandwich complexes with η^9, η^5-indenyl ligands were isolated.[8] Replacing one of the isopropyl groups with a methyl substituent in mixed pentamethylcyclopentadienyl (Cp*), indenyl compounds reduced the steric protection of the Zr, allowed dimerization, and resulted in isolation of weakly activated end-on and side-on, end-on dinitrogen complexes that are subject to N₂ loss.[9] Inspired by these observations, the chemistry of the homoleptic bis(indenyl)zirconium complexes was explored.

Sodium amalgam reduction of a pentane or toluene solution of a *rac/meso*-mixture of $(\eta^5$-C₉H₅-1-ⁱPr-3-Me)₂ZrCl₂ (**1-Cl₂**) under Ar or vacuum resulted in isolation of the bis(indenyl)zirconium sandwich compound, **1**, as an equimolar mixture of diastereomers (Figure 1). Dark burgundy **1** exhibited ¹H and ¹³C NMR spectroscopic features diagnostic of η^9 indenyl hapticity.[8] The sandwich structure was also confirmed by X-ray diffraction (Figure 2).

Performing the Na(Hg) reduction of **1-Cl₂** under N₂ produced a different outcome. Recrystallization of the red product from pentane furnished a crystalline solid identified as the bis(indenyl)zirconium end-on dinitrogen compound, **[1-NaCl]₂N₂**, with inclusion of 1 equiv of NaCl per Zr (Figure 1). Only the *meso* diastereomer of the metallocenes was observed in the solid state; similar selectivity was also observed in the crystal structure of **1**. Reactivity studies establish the presence of *rac* zirconocene subunits in bulk samples of the compound (*vide infra*).

The overall solid state structure of **[1-NaCl]₂N₂** (Figure 2) consists of four zirconocenes, comprised of two dimers bridged by interactions between Na atoms with neighboring chlorides (see Supporting Information (SI) for additional structural details). The metrical parameters of **[1-NaCl]₂N₂** establish a more strongly activated N₂ ligand than those found in the previously reported
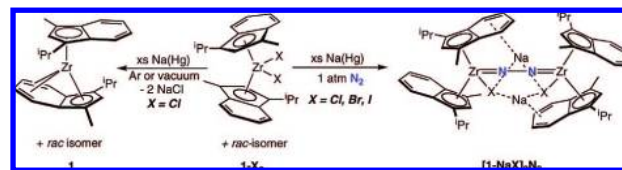

Figure 1. Synthesis of **1** and **[1-NaX]₂N₂** compounds.

mixed Cp*, indenyl dinitrogen compounds with weakly activated end-on or side-on, end-on N₂ ligands.[9] In these cases, the weak activation is a consequence of η^2 or η^4 benzo ring coordination. For **[1-NaCl]₂N₂**, the Zr=N bond lengths of 1.878(3) Å are only slightly longer than those reported for crystallographically characterized zirconium imido[10] compounds, such as $(\eta^5$-C₅H₅)₂Zr(NⁱBu)THF ($d_{Zr=N}$ = 1.826(4) Å).[11] The N(1)−N(1A) distance of 1.352(5) Å approaches the value 1.377(3) Å found in $[(\eta^5$-C₅Me₄H)₂Zr]₂(μ_2, η^2, η^2-N₂).[4c] The increased reduction of the bridging N₂ ligand is likely a result of the coordination of the benzo rings to the Na rather than the Zr, allowing increased metal−ligand backbonding.

The observation of NaCl inclusion with **[1-NaCl]₂N₂** prompted reduction of the bis(indenyl)zirconium dibromide (**1-Br₂**) and diiodide (**1-I₂**) compounds. Using a similar synthetic procedure, two additional dinitrogen compounds, **[1-NaBr]₂N₂** and **[1-NaI]₂N₂**, were isolated (Figure 1). Crystallographic characterization of **[1-NaI]₂N₂** established a similar core structure to the chloride congener. Both the Zr=N and N−N distances of 1.901(2) and 1.316(5) Å are consistent with a modestly activated, end-on dinitrogen compound. These values are slightly less pronounced than those found in **[1-NaCl]₂N₂**, demonstrating the coordinated halide attenuates the reduction potential of the metal center. The different radii of the respective halogens may also be important. Unlike the chloride compound, **[1-NaI]₂N₂** is dimeric and does not exhibit interactions with neighboring dimers. As presented in the SI, the metrical parameters of the indenyl rings establish no reduction unlike in sandwich **1** and other indenyl dinitrogen compounds with η^2 or η^4 benzo interactions.[8,9]

The ¹H NMR spectra of the three activated end-on dinitrogen compounds are broad and relatively uninformative, likely due to salt inclusion. EPR spectroscopy and magnetic susceptibility measurements establish diamagnetic molecules free of paramagnetic impurities; variable temperature NMR experiments produced no gross changes.

N₂ coordination in bulk samples was confirmed by combustion analysis and reactivity studies. Treatment of **[1-NaCl]₂N₂** with an excess of either PbCl₂ or I₂ furnished the zirconocene dihalide (**1-Cl₂** or **1-I₂**) along with 91 and 95% of the expected N₂ gas (Toepler pump), respectively. Likewise, protonation of **[1-NaCl]₂N₂** with excess H₂O or HCl yielded 96 and 45% of the expected hydrazine and no NH₃. Reduction of N₂ to hydrazine with weak Brønsted acids is typically reserved for strongly activated N₂ compounds.[12,13]
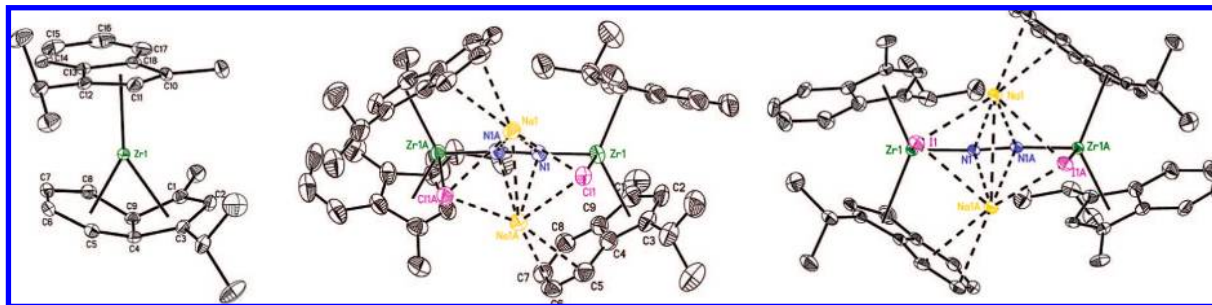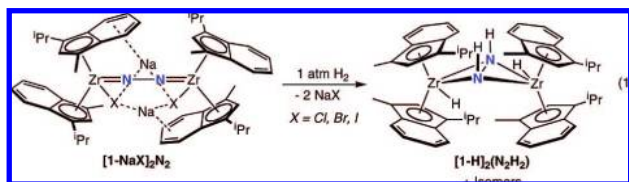
Figure 2. Molecular structures of **1** (left), **[1-NaCl]₂N₂** (middle), and **[1-NaI]₂N₂** (right) at 30% probability ellipsoids.

With a new class of activated end-on zirconocene dinitrogen compounds in hand, N₂ hydrogenation was explored. Exposure of a benzene-d_6 solution of **[1-NaCl]₂N₂**, **[1-NaBr]₂N₂**, or **[1-NaI]₂N₂** to 1 atm of H₂ yielded the hydrido zirconocene hydrazido compound **[1-H]₂(N₂H₂)**, concomitant with salt elimination (eq 1). Thus, side-on coordination, at least in the ground state, is not a necessary condition for N₂ hydrogenation.

For each compound, the hydrogenation reaction was accompanied by variable amounts of decomposition, as free indenyl ligand was observed by ¹H NMR spectroscopy. Pure **[1-H]₂(N₂H₂)** was best obtained from the hydrogenation of the iodo derivative and the free indenyl ligand removed by washing with copious amounts of cold pentane. NMR and IR spectroscopy, combustion analysis (no N₂ loss), and reactivity studies confirmed N−H bond formation. For example, a N−H stretch was observed at 3238 cm⁻¹ in the solid state IR spectrum of **[1-H]₂(N₂H₂)**. This band shifts appropriately to 2403 cm⁻¹ upon treatment with D₂ to yield **[1-D]₂(N₂D₂)**.

The presence of both *rac* and *meso* diastereomers coupled with Zr−H and N−H bond formation produces additional stereochemistry and yields at least 10 isomers of **[1-H]₂(N₂H₂)**.[14] As a result, the NMR spectrum of **[1-H]₂(N₂H₂)** is exceedingly complex. Both ¹H−¹⁵N HSQC and HMBC experiments were used to assign the N−H, Zr−H, and ¹⁵N resonances and identified formation of 10 isomers (see SI). The observation of upfield shifted N−*H* peaks in the vicinity of −0.81 to −1.44 ppm coupled with the observation of ¹⁵N shifts from ~92 to 98 ppm signals the presence of η^2,η^2-N₂H₂ ligands; no downfield resonances diagnostic of end-on haptomers were detected.[12] Based on two bond coupling, terminal Zr−H peaks were assigned between 4.52 and 4.81 ppm.

The crown ethers 18-crown-6 and 15-crown-5 and excess THF were added to benzene-d_6 solutions of **[1-NaCl]₂N₂** in an attempt to sequester the Na ions. In all cases, mixtures of both soluble and insoluble products were observed by ¹H NMR spectroscopy. In the case of 18-crown-6, one insoluble product **{Na[1-Cl]₂N₂}Na(18-c-6)₁.₅** was characterized by X-ray diffraction and contains a modestly activated N₂ ligand (see SI). Importantly only one Na ion was removed from the coordination sphere of the Zr. Exposure of these mixtures to an H₂ atmosphere produced no N−H bond formation. The lack of hydrogenation of **{Na[1-Cl]₂N₂}Na(18-c-6)₁.₅** is likely a result of its poor solubility, as N₂H₄ was observed

upon hydrolysis. For the other products, it is likely that both Na ions are sequestered, as no N₂H₄ was formed upon hydrolysis, suggesting weak N₂ activation.

In summary, a new class of activated end-on bis(indenyl)zirconium dinitrogen complexes has been synthesized and structurally characterized. Interactions between the included Na ions and the indenyl benzo substituents prevent ring coordination to Zr, increasing metal−N₂ backbonding. The successful hydrogenation of these compounds demonstrates that end-on coordination in the ground state is a viable pathway for the 1,2-addition of 2 equiv of H₂. These observations raise the possibility of η^2,η^2 to η^1,η^1 isomerization as a potential mechanism in the hydrogenation of side-on zirconocene dinitrogen compounds.[5]

Supporting Information Available: Complete experimental procedures, selected NMR spectra and crystallographic data for **1**, **[1-NaCl]₂N₂**, **[1-NaI]₂N₂**, and **{Na[1-Cl]₂N₂}Na(18-c-6)₁.₅** (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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