

# Ammonia Synthesis by Hydrogenolysis of Titanium–Nitrogen Bonds Using Proton Coupled Electron Transfer

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**S** Supporting Information

**ABSTRACT:** The catalytic hydrogenolysis of the titanium–amide bond in  $(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ti}(\text{Cl})\text{NH}_2$  to yield free ammonia is described. The rhodium hydride,  $(\eta^5\text{-C}_5\text{Me}_5)(\text{py-Ph})\text{RhH}$  (py-Ph = 2-phenylpyridine), serves as the catalyst and promotes N–H bond formation via hydrogen atom transfer. The N–H bond dissociation free energies of ammonia ligands have also been determined for titanocene and zirconocene complexes and reveal a stark dependence on metal identity and oxidation state. In all cases, the N–H BDFEs of coordinated  $\text{NH}_3$  decreases by >40 kcal/mol from the value in the free gas phase molecule.

The interconversion of ammonia,  $\text{NH}_3$ , with its constituent elements  $\text{N}_2$  and  $\text{H}_2$ , is a long-standing challenge in chemical synthesis and is attractive for the development of alternative energy schemes with reduced fossil fuel dependencies and carbon footprints.<sup>1</sup> Batch rather than continuous ammonia synthesis at low pressure, for example, may prove more compatible with renewable hydrogen and also enable  $\text{NH}_3$  to serve as a fuel or  $\text{H}_2$  storage medium.<sup>2</sup> Proton coupled electron transfer (PCET),<sup>3</sup> a pathway operative in enzymatic ammonia synthesis,<sup>4</sup> is an attractive strategy for N–H bond formation under mild conditions. Molecular molybdenum catalysts such as those independently reported by Schrock<sup>5</sup> and Nishibayashi<sup>6</sup> rely on pyridinium acids in conjunction with strong reducing agents to affect ammonia synthesis and may involve PCET reactions for N–H assembly.<sup>7</sup> Elucidation and optimization of these pathways may ultimately result in catalysts with longer lifetimes that operate with reduced overpotential.

For such an approach to be feasible, a detailed understanding of N–H bond dissociation free energies (BDFEs) must be determined. Despite considerable efforts over the past five decades in homogeneous  $\text{N}_2$  reduction, surprisingly few thermochemical data are available for intermediates relevant to ammonia synthesis. Here we describe experimental and computational determination of N–H BDFEs as a function of the transition metal and oxidation state for titanocene and zirconocene complexes and demonstrate the utility of PCET reactions in ammonia synthesis and breaking strong M–N bonds in early transition metal compounds.

Dating to Vol'pin and Shur's seminal work on ammonia synthesis, group 4 metallocenes have a rich  $\text{N}_2$  fixation chemistry.<sup>8</sup> Our laboratory has since demonstrated an array of  $\text{N}_2$  cleavage and functionalization reactions coupled to

N–H<sup>9</sup> and N–C<sup>10</sup> bond formation with appropriately substituted zirconocene and hafnocene complexes.<sup>11</sup> One significant challenge in this chemistry is removing the functionalized nitrogen ligand from the coordination sphere of the azaphilic early transition metal. Strong acids or silylating agents are often required for liberation of the desired product and generate metal products incompatible with catalytic turnover. Alternative methods, such as PCET,<sup>12</sup> for M–NR<sub>n</sub> bond hydrogenolysis are attractive as this linkage is typically unreactive toward  $\text{H}_2$ .<sup>13</sup>

To explore whether PCET was a viable strategy for liberation of ammonia from the coordination sphere of a group 4 metallocene, the sterically protected chlorotitanocene and -zirconocene parent amide complexes,  $(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{M}(\text{Cl})\text{NH}_2$  (1-(Cl)NH<sub>2</sub>, M = Ti; 2-(Cl)NH<sub>2</sub>, M = Zr) were prepared and crystallographically characterized (see Supporting Information (SI)). Initial experiments focused on the determination of the pK<sub>a</sub> and redox potential of the protonated complexes to provide an experimental measure of the N–H BDFE of coordinated  $\text{NH}_3$  as a function of metal. Treatment of either 1-(Cl)NH<sub>2</sub> or 2-(Cl)NH<sub>2</sub> with HBAR<sup>F</sup><sub>4</sub> (Ar<sup>F</sup> = C<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub>) yielded the ammonia complexes,  $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{M}(\text{Cl})\text{NH}_3]\text{BAR}^{\text{F}}_4$  ([1-(Cl)NH<sub>3</sub>]<sup>+</sup>, M = Ti, [2-(Cl)NH<sub>3</sub>]<sup>+</sup>, M = Zr). These compounds were crystallographically characterized and readily characterized via <sup>1</sup>H NMR in polar noncoordinating solvents such as CD<sub>2</sub>Cl<sub>2</sub>; stronger donor media such as THF resulted in  $\text{NH}_3$  dissociation.

The acidities of both cationic ammonia complexes were determined in 2-methyl-THF (MeTHF) solution as  $\text{NH}_3$  dissociation was not observed in this solvent and pK<sub>ip</sub> (where pK<sub>ip</sub> represents the ion-pair acidity) values for an array of bases are known in THF solution.<sup>14</sup> Titrations with an appropriate base were monitored by UV–vis spectroscopy as the acid and conjugate base pair for both titanium and zirconium compounds were readily discerned. Both complexes were rapidly deprotonated by pyrrolidine (pK<sub>ip</sub>, THF = 15.3) and yielded 1-(Cl)NH<sub>2</sub> or 2-(Cl)NH<sub>2</sub> as the sole organometallic products. No reaction was observed with NEt<sub>3</sub> (pK<sub>ip</sub>, THF = 14.1). A competition experiment was also performed whereby [1-(Cl)NH<sub>3</sub>]<sup>+</sup> was mixed with 2-(Cl)NH<sub>2</sub> and allowed for the determination of a ΔpK<sub>ip</sub> of –0.3 between the two compounds. Individual titration experiments with pyrrolidine yielded pK<sub>ip</sub> values for [1-(Cl)NH<sub>3</sub>]<sup>+</sup> and [2-(Cl)NH<sub>3</sub>]<sup>+</sup> of 15.0 and 14.7, respectively.

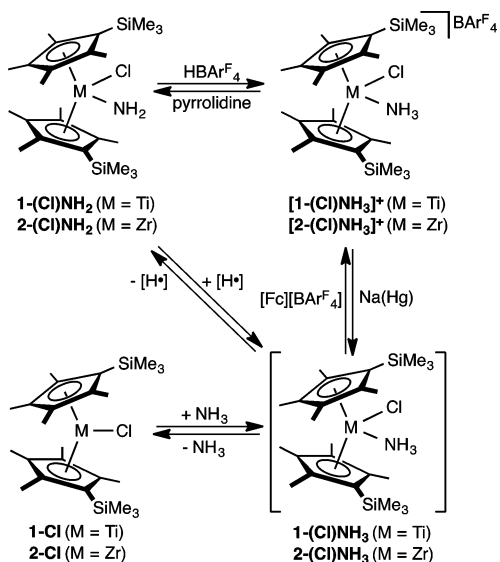
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Cyclic voltammetry was also carried out on MeTHF solutions of  $[1-(\text{Cl})\text{NH}_3]^+$  and  $[2-(\text{Cl})\text{NH}_3]^+$  with 0.10 M  $[\text{tBu}_4\text{N}][\text{BAR}^{\text{F}}_4]$  as the electrolyte. Irreversible waves were observed with cathodic peak potentials at  $-1.60$  V (Ti) and  $-2.32$  V (Zr) vs  $\text{Fc}/\text{Fc}^+$ ; the observed irreversibility is a result of  $\text{NH}_3$  dissociation upon reduction (*vide infra*). Chemical reduction of both compounds was accomplished using stoichiometric 0.5%  $\text{Na}(\text{Hg})$  ( $E^0 = -2.36$  V vs  $\text{Fc}/\text{Fc}^+$ ) and resulted in the isolation of the titanocene(III) and zirconocene(III) chloride complexes, **1-Cl** and **2-Cl**, respectively. Both compounds were characterized by solution EPR spectroscopy at  $23$  °C and exhibited isotropic signals with  $g_{\text{iso}}$  values of 1.953 (Ti) and 1.937 (Zr). **2-Cl** was also independently synthesized and characterized by X-ray diffraction and is a rare example of a monomeric Zr(III) complex.<sup>15</sup> Formation of free ammonia obtained from the reduction reaction was confirmed by indophenolic titration.<sup>16</sup>

Experiments were also conducted to evaluate the coordination of ammonia to the metallocene(III) chloride complexes. Monitoring the addition of excess  $\text{NH}_3$  gas to **1-Cl** or **2-Cl** by X-band EPR spectroscopy at  $23$  °C produced new features at  $g_{\text{iso}} = 1.979$  (Ti) and 1.970 (Zr) that restored to the original values upon evacuation. Formation of similar aquo complexes of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}$  have also been previously observed.<sup>17</sup> Addition of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{BAR}^{\text{F}}_4]$  to MeTHF solutions of **1-Cl** and **2-Cl** in the presence of excess  $\text{NH}_3$  gas furnished  $[1-(\text{Cl})\text{NH}_3]^+$  and  $[2-(\text{Cl})\text{NH}_3]^+$ , respectively as determined by  $^1\text{H}$  NMR spectroscopy. These experiments complete a sequence of reversible proton and electron transfer events linking the metal–amide complexes with ammonia (Scheme 1).

### Scheme 1. Transformations Relevant to Proton Coupled Electron Transfer (PCET) for Titanocene and Zirconocene Complexes



The impact of the metal oxidation state on the proton and electron transfer properties of amide complexes was also examined. The titanocene(III) amide complex, **1-NH<sub>2</sub>**,<sup>18</sup> was prepared, crystallographically characterized, and treated with  $\text{HBAR}^{\text{F}}_4$  and yielded the cationic titanium(III) ammonia complex,  $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{TiNH}_3][\text{BAR}^{\text{F}}_4]$  ( $[1-\text{NH}_3]^+$ ). Deprotonation of this compound required the stronger base, 1,8-diazabicycloundec-7-ene (DBU,  $\text{p}K_{\text{ip}}$ , THF = 17.8). Equilibra-

tion of  $[1-\text{NH}_3]^+$  with **1-(Cl)NH<sub>2</sub>** established a  $\Delta\text{p}K_{\text{ip}}$  of 1.2 with the titanium(III) complex being more basic. A cyclic voltammogram of  $[1-\text{NH}_3]^+$  exhibited an irreversible wave with a peak cathodic peak potential at  $-2.60$  V. The observed irreversibility is likely a result of N–H oxidative addition upon reduction to Ti(II).<sup>19</sup>

It is instructive to compare the  $\text{p}K_{\text{ip}}$  and electrochemical data of  $[1-(\text{Cl})\text{NH}_3]^+$ ,  $[2-(\text{Cl})\text{NH}_3]^+$ , and  $[1-\text{NH}_3]^+$ . While selected examples of measurements of N–H BDFEs have been reported for the interconversion of metal-imido to metal-amido compounds,<sup>12</sup> much less is known about M–NH<sub>2</sub> derivatives en route to  $\text{NH}_3$ . This absence of data is due, in part, to the paucity of parent amido compounds. For titanocenes and zirconocenes in this study, absolute BDFEs cannot be determined because of the irreversible electrochemical behavior and the lack of a known correction value for the H atom in 2-MeTHF solution.<sup>3b</sup> To overcome this limitation, relative BDFEs among **1-(Cl)NH<sub>2</sub>**, **2-(Cl)NH<sub>2</sub>**, and **1-NH<sub>2</sub>** are nevertheless useful and can be calculated according to eq 2:<sup>20</sup>

$$\text{BDFE} = 1.37(\text{p}K_{\text{ip}}) + 23.06E_{\text{red}} + C \quad (1)$$

$$\Delta\text{BDFE} = 1.37\Delta\text{p}K_{\text{ip}} + 23.06\Delta E_{\text{red}} \quad (2)$$

Table 1 reports the compilation of physical data measured for the metallocene amide compounds. The data assume similar

**Table 1. Summary of Physical Data for Titanocene and Zirconocene Amide Complexes (BDFEs reported in kcal/mol)**

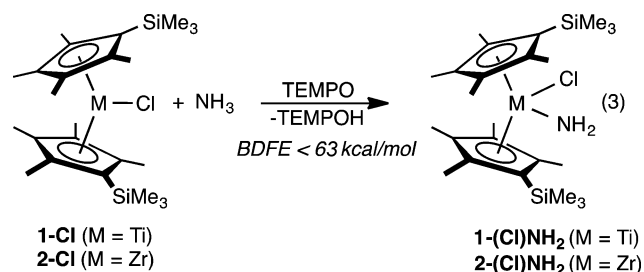
compd	$E_{\text{pc}}$ (V) <sup>a</sup>	$\text{p}K_{\text{ip}}$ <sup>b</sup>	$\Delta\text{BDFE}^c$ (exptl)	BDFE <sup>d</sup> (calcd)
$[1-(\text{Cl})\text{NH}_3]^+$	$-1.60$	15.0	–	61
$[2-(\text{Cl})\text{NH}_3]^+$	$-2.32$	14.7	$-17$	41
$[1-\text{NH}_3]^+$	$-2.60$	16.2	$-21$	42

<sup>a</sup>Peak cathodic potential reported relative to  $\text{Fc}/\text{Fc}^+$  in Me–THF solution with 0.10 M  $[\text{tBu}_4\text{N}][\text{BAR}^{\text{F}}_4]$  as the electrolyte. <sup>b</sup>Ion-pair acidity determined by UV/vis titration against standards in Me–THF. <sup>c</sup>Defined as  $\text{BDFE}(2-(\text{Cl})\text{NH}_3) - \text{BDFE}(1-(\text{Cl})\text{NH}_3)$  and  $\text{BDFE}(1-\text{NH}_3) - \text{BDFE}(1-(\text{Cl})\text{NH}_3)$  using eq 2. <sup>d</sup>Calculated free energy change for the reaction of  $[\text{M}]\text{NH}_2\text{–H} \rightarrow [\text{M}]\text{NH}_2 + \text{H}^\bullet$ .

ion-pairing effects and utilize peak cathodic potentials ( $E_{\text{pc}}$ ) due to the observed electrochemical irreversibility. Given the structural similarity of the compounds and the constant solvent medium, it is likely these assumptions have little impact on the relative N–H BDFE values. Also reported in Table 1 are full molecule DFT-computed N–H BDFEs for each compound.

Several trends are evident. Coordination of ammonia to titanium or zirconium reduces the BDFE by  $>40$  kcal/mol compared to the gas phase bond strength of 99.4 kcal/mol of free ammonia.<sup>3b</sup> Similar weak E–H bonds of 49.4 and 65.0 have been computed for the coordination of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  to  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}$ , respectively.<sup>21</sup> The BDFEs vary within the series where changing the titanium oxidation state from 4+ to 3+ greatly reduces the N–H bond strength. Likewise, moving from Ti(IV) to Zr(IV) has a similar bond-weakening impact. Importantly, the  $\text{p}K_{\text{ip}}$  values within the series exhibit little variance; the observed decrease in BDFE as a function of metal or oxidation state is therefore dominated by the change in redox potential. It is also apparent from the calculated BDFE values that the titanium(IV) derivative, **1-(Cl)NH<sub>2</sub>**, is the most promising for liberation of ammonia by PCET.

H atom abstraction experiments were conducted to validate these findings. Addition of  $\text{NH}_3$  gas to a benzene- $d_6$  solution containing 1-Cl or 2-Cl and 1 equiv of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) resulted in immediate formation of the chlorometalocene amide compounds, 1-(Cl) $\text{NH}_2$  or 2-(Cl) $\text{NH}_2$ , and TEMPO-H (eq 3) quantitatively as determined



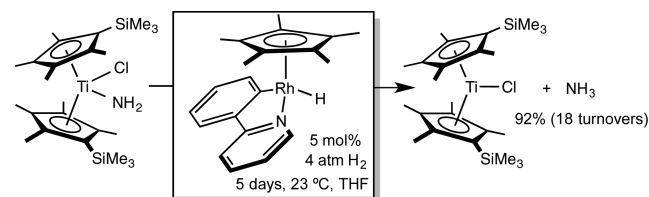
by  $^1\text{H}$  NMR spectroscopy. Control experiments whereby  $\text{NH}_3$  gas was added to a benzene- $d_6$  of TEMPO produced no reaction. As the BDFE of TEMPO-H in benzene is 65.2 kcal/mol,<sup>3b</sup> and the chlorometalocene amide complexes are generated in greater than 95% yield, these experiments establish an N-H BDFE of <63 kcal/mol upon coordination of ammonia to Ti(III) or Zr(III). Similar experimental verification has been provided from observation of HAT chemistry from addition of  $^n\text{OctNH}_2$  to  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}$  in the context of epoxide ring opening.<sup>21</sup>

Attention was then devoted to ammonia synthesis from 1-(Cl) $\text{NH}_2$  using PCET. Stirring a THF- $d_8$  solution of 1-(Cl) $\text{NH}_2$  under 4 atm of  $\text{H}_2$  for 5 days at 23 °C produced no change, highlighting the strength of the Ti-NH<sub>2</sub> interaction and lack of a kinetic pathway for hydrogenolysis. We reasoned that addition of an appropriate metal complex with an M-H bond strength less than 61 kcal/mol would enable PCET and liberate ammonia from the coordination sphere of the titanium. Additionally, if the metal complex were chosen such that the weak M-H bond could be regenerated under an atmosphere of  $\text{H}_2$ , the PCET could be rendered catalytic. Norton and co-workers have recently reported  $(\eta^5\text{-C}_5\text{Me}_5)(\text{py-Ph})\text{RhH}$  (Rh-H; py-Ph = 2-pyridylphenyl), an attractive PCET reagent as the Rh-H BDFE was measured to be 52.3 kcal/mol.<sup>22</sup> Significantly, the Rh-H complex was demonstrated to be operative for catalytic PCET under an atmosphere of  $\text{H}_2$ .

The feasibility of this approach was evaluated in a series of stoichiometric experiments whereby 1 equiv of Rh-H was added to each of the metallocene amides, 1-(Cl) $\text{NH}_2$ , 2-(Cl) $\text{NH}_2$ , and 1-NH<sub>2</sub>, in THF- $d_8$  solution. As expected from the physical measurements, both 2-(Cl) $\text{NH}_2$  and 1-NH<sub>2</sub> produced no reaction even upon heating to 60 °C for 24 h. Monitoring the reaction with 1-(Cl) $\text{NH}_2$  by  $^1\text{H}$  NMR spectroscopy established the disappearance of the Rh-H resonance at -12.5 ppm along with the peaks for the diamagnetic titanium complex over the course of 6 h. Analysis of the reaction volatiles at this time point established a 98% yield of free ammonia while treatment of the organometallic residue with HCl resulted in 95% recovery of 1-Cl<sub>2</sub>, implicating paramagnetic 1-Cl as the sole product following ammonia release. The fate of the rhodium is likely paramagnetic  $[(\eta^5\text{-C}_5\text{Me}_5)(\text{py-Ph})\text{Rh}]$  as addition of  $\text{H}_2$  to the reaction mixture following hydrogen atom transfer cleanly regenerated Rh-H, implicating its formation.

Ammonia synthesis in the presence of catalytic quantities of Rh-H was also explored (Scheme 2). Hydrogenation of 1-

## Scheme 2. Generation of Ammonia from Catalytic Hydrogenolysis of 1-(Cl) $\text{NH}_2$ in the Presence of 5 mol % Rh-H



(Cl) $\text{NH}_2$  with 4 atm of  $\text{H}_2$  in the presence of 5 mol % of Rh-H yielded  $92 \pm 6\%$  of  $\text{NH}_3$  over the course of 5 days, corresponding to 18 turnovers based on rhodium. Rhodium loadings as low as 1 mol % were also effective but proved irreproducible. Repeating the catalytic hydrogenations with 2-(Cl) $\text{NH}_2$  and 1-NH<sub>2</sub> and 5 mol % of Rh-H produced no reaction.

Comparison of redox potentials eliminates the possibility that the catalytic hydrogenolysis of the Ti-NH<sub>2</sub> bond in 1-(Cl) $\text{NH}_2$  proceeds via initial electron transfer. The oxidation potential of Rh-H in THF has been reported as -0.38 V vs Fc/Fc<sup>+</sup>, which is well below the potential of -2.8 V required to reduce 1-(Cl) $\text{NH}_2$  (see SI). Likewise, the  $\text{p}K_{\text{ip}}$  of [Rh]-H is ~20, which is well above the  $\text{p}K_{\text{ip}}$  of 1-(Cl) $\text{NH}_2$  (*vide supra*).<sup>23</sup> The relatively high barriers for both initial proton and initial electron transfer from Rh-H to 1-(Cl) $\text{NH}_2$  implicate concerted hydrogen atom transfer as the most likely pathway for catalytic ammonia formation from 1-(Cl) $\text{NH}_2$ .

In summary, we have demonstrated the utility of proton coupled electron transfer as a method for the liberation of ammonia from the coordination sphere of an early transition metal. In the presence of an appropriate metal catalyst, hydrogen can be used as the stoichiometric H atom source providing an attractive method for product release following small molecule activation and functionalization.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details; computational details; electrochemical characterization of [1-(Cl) $\text{NH}_3$ ]<sup>+</sup>, [2-(Cl) $\text{NH}_3$ ]<sup>+</sup>, [1-NH<sub>3</sub>]<sup>+</sup>, and 1-(Cl) $\text{NH}_2$ ; EPR spectra of 1-(Cl) $\text{NH}_3$ , 2-(Cl) $\text{NH}_3$ , 1-NH<sub>2</sub>, [1-NH<sub>3</sub>]<sup>+</sup>, and 2-Cl; crystallographic data for 1-(Cl) $\text{NH}_2$ , 2-(Cl) $\text{NH}_2$ , 1-NH<sub>2</sub>, [1-(Cl) $\text{NH}_3$ ]<sup>+</sup>, [2-(Cl) $\text{NH}_3$ ]<sup>+</sup>, [1-NH<sub>3</sub>]<sup>+</sup>, and 2-Cl in cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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(14)  $pK_{ip}$  is the apparent acidity of a complex in a nonpolar medium in which ion pairing is significant. As these experiments were conducted in MeTHF ( $\epsilon_r = 6.97$ ),  $pK_{ip}$  is the most appropriate way to denote the apparent acidity. A correction for ion pairing, such as the Fuoss equation, was not employed and would not be expected to have a significant impact on the relative acidities due to similar ion-pairing effects among the complexes under investigation. For reference  $pK_{ip}$  data and further explanation, see: (a) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019. (b) Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2002**, *67*, 1873.

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