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Coupled  
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## Evaluation of Excited State Bond Weakening for Ammonia Synthesis from a Manganese Nitride: Stepwise Proton Coupled Electron Transfer is Preferred over Hydrogen Atom Transfer

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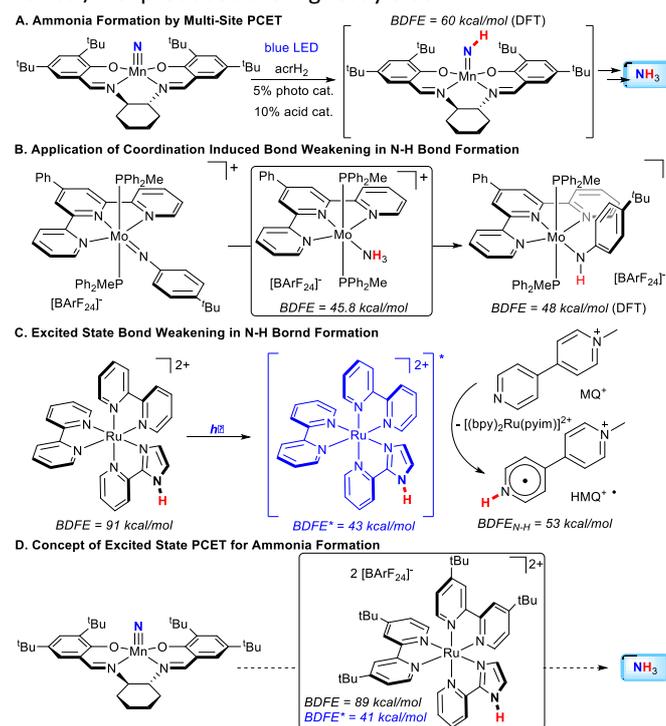
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Concepts for the thermodynamically challenging synthesis of weak N-H bonds by photoinduced proton coupled electron transfer are explored. Upon irradiation with blue light, ammonia synthesis was achieved from the manganese nitride (<sup>t</sup>BuSalen)MnN (<sup>t</sup>BuSalen = (S,S)-(+)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) in the presence of 9,10-dihydroacridine and a ruthenium photocatalyst in <sup>t</sup>PrOH solution. Although in one case the ruthenium complex bears a remote N-H bond that weakens to 41 kcal/mol upon irradiation, control experiments with the *N*-methylated analog demonstrate the ruthenium complex serves as a photoreductant rather than hydrogen-atom transfer catalyst in aprotic solvents. Luminescence quenching experiments support a ruthenium(II)/(III) cycle rather than a ruthenium(I)/(II) alternative. Identification of the manganese complex following ammonia synthesis was also accomplished.

The formation of weak chemical bonds near thermodynamic potential is a long-standing challenge in chemical synthesis. This concept is particularly relevant to nitrogen fixation with molecular transition metal catalysts where weak N-H bonds, many below the thermodynamic threshold relative to H<sub>2</sub> formation (48 kcal/mol), are formed during the catalytic cycle.<sup>1</sup> State-of-the-art methods rely on combinations of strong acids and reductants and are accompanied by a large chemical overpotential, in some cases close to 300 kcal/mol, that drives the ammonia synthesis reaction.<sup>1a-c, 2</sup> Photodriven proton-coupled electron transfer (PCET) is an attractive method for the synthesis of weak N-H bonds near thermodynamic equilibrium as energy from visible light is converted with the aid of a photocatalyst to drive the formation of weak bonds. Photodriven PCET methods have recently been applied to both C-C bond-forming<sup>3</sup> and -cleavage reactions.<sup>4</sup> This approach was also extended to N-H bond

formation and ultimately ammonia synthesis from the manganese nitride (<sup>t</sup>BuSalen)MnN (<sup>t</sup>BuSalen = (S,S)-(+)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine), where the first N-H bond formation was computed to be  $\Delta G = -60$  kcal/mol (Figure 1, A).<sup>5</sup> Use of 9,10-dihydroacridine (acrH<sub>2</sub>) as terminal proton and electron source and an appropriately matched photoredox catalyst and weak Brønsted acid with effective bond dissociation free energies (BDFEs) between 35–46 kcal/mol produced the highest yields.



**Figure 1.** A: Photodriven proton coupled electron transfer using 9,10-dihydroacridine (acrH<sub>2</sub>), an appropriately matched photocatalyst and Brønsted acid. B: Application of coordination-induced bond weakening in N-H bond formation. C: Excited state bond weakening in the formation of weak N-H bonds. D: Concept of excited state bond weakening as applied to N-H bond formation and ammonia synthesis.

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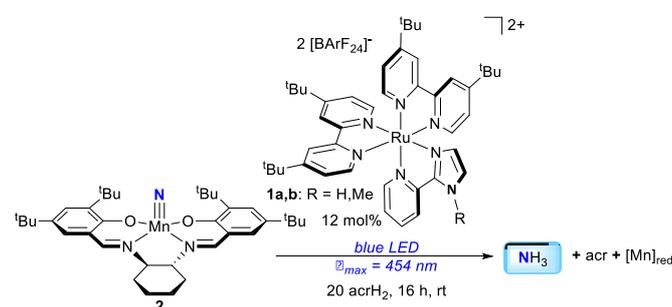
An alternative strategy relies on coordination-induced bond weakening whereby coordination of a ligand to a transition metal dramatically alters the BDFE of an element-hydrogen bond.<sup>6</sup> This concept has been demonstrated in the ground state, whereby the non-classical ammine complex, [(<sup>Ph</sup>Tpy)(PPh<sub>2</sub>Me)<sub>2</sub>Mo(NH<sub>3</sub>)]<sup>6-7</sup> (<sup>Ph</sup>Tpy = 4'-Ph-2,2',6',2''-terpyridine; [BARF<sub>24</sub>]<sup>-</sup> = tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate) undergoes H<sub>2</sub> loss upon thermolysis and also serves as a hydrogen-atom donor for both N-H<sup>6b</sup> (Figure 1B) and C-H<sup>7</sup> bond forming reactions. While useful as reagents, the thermal instability of these complexes coupled with competing H<sub>2</sub> formation makes them challenging to handle and ultimately pose barriers for rendering them catalytic. One possibility to avoid these limitations is to use complexes that in the ground state have sufficiently strong N-H bonds to avoid H<sub>2</sub> formation but upon excitation undergo bond weakening and ultimately proton coupled electron transfer (Figure 1C). Demonstration of the concept has been pioneered by Wenger with ruthenium complexes bearing remote N-H bonds that upon irradiation undergo PCET to *N*-methyl-4,4'-bipyridinium (MQ<sup>+</sup>) or 1,4-benzoquinone forming the spectroscopically observed corresponding radical cation HMQ<sup>•+</sup> or the corresponding semiquinone, respectively.<sup>8</sup> Another attractive feature of these compounds is tuning of the excitation wavelength and excited state N-H BDFE through rational ligand alterations. Here we describe exploration of this concept to N-H bond formation relevant to ammonia synthesis from the manganese nitride, (<sup>t</sup>Bu<sub>4</sub>Salen)MnN.

The manganese nitride (<sup>t</sup>Bu<sub>4</sub>Salen)MnN **2** was selected as the substrate for these studies due to the relevance of transition metal nitrides in ammonia formation as well as oxidation,<sup>1d, 2a-c,9</sup> its ease of synthesis,<sup>10</sup> the relatively high BDFE calculated for the corresponding imido complex and established ammonia synthesis chemistry by multi-site PCET.<sup>5</sup> Two ruthenium complexes with and without pendant N-H bonds, **1a** and **1b**, were synthesized (Scheme S1) to explore excited state PCET chemistry. Specifically, the *N*-methylated variant, **1b** was prepared for control experiments. Wenger has previously reported the [PF<sub>6</sub>]<sup>-</sup> derivative of **1a** and measured a ground state N-H BDFE of 89 kcal/mol that decreases to a value of 41 kcal/mol upon irradiation to the excited state.<sup>8b</sup> Compared to the three N-H bond forming steps required for ammonia synthesis from **2** (60 kcal/mol, 84 kcal/mol, 85 kcal/mol, respectively),<sup>5</sup> suggests that ammonia formation should occur under irradiation with visible light, while no reactivity is expected in the ground state. The [BARF<sub>24</sub>]<sup>-</sup> complex was prepared for the present study to improve solubility and to minimize any potential complications from ion pairing. The benzene-*d*<sub>6</sub> <sup>1</sup>H NMR spectrum of **1a** is analogous to that reported for the [PF<sub>6</sub>]<sup>-</sup> derivative, suggesting little perturbation by the anion exchange and likely little alteration to the N-H bond energetics.

Initial experiments were conducted with the manganese nitride **2** as the substrate with **1a** as the excited state PCET photocatalyst along with a selection of potential stoichiometric proton and electron sources: 9,10-dihydroacridine (acrH<sub>2</sub>), 9,10-dihydroanthracene (DHA), 1,4-cyclohexadiene (CHD) and

diethyl-1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch ester, HEH). The results of these studies are reported in Table S1.<sup>11</sup> Consistent with their low acidities, DHA (pK<sub>a</sub> = 30.1 in DMSO)<sup>12</sup> and CHD (pK<sub>a</sub> expected to be similar to DHA) produced only 2 % ammonia even when used in excess (20 equivalents). With HEH (pK<sub>a</sub> = 19.8 in DMSO),<sup>13</sup> 7% ammonia was observed when both 1.5 and 20 equiv were used, but the conversion of **2** increased (Table S1). Using 1.5 equivalents of acrH<sub>2</sub> (pK<sub>a</sub> = 25.2 in DMSO)<sup>14</sup> produced 10% free NH<sub>3</sub>, a value that increased to 80% when 20 equivalents were used (Tables S1 and S2).<sup>11</sup> It is likely that increasing the number of equivalents of the proton-electron source increases the rate of N-H bond formation, if the reagent is above the thermodynamic threshold for the ammonia synthesis reaction.

**Table 1.** Formation of ammonia from the manganese nitride **2** using photo-induced PCET.



entry	light	acrH <sub>2</sub>	[Ru]	NH <sub>3</sub> [%]			
				<b>1a</b> (R = H)		<b>1b</b> (R = Me)	
				<sup>i</sup> PrOH	THF	<sup>i</sup> PrOH	THF
1	✓	✓	✓	80	62	72	80
2	—	✓	✓	3 <sup>[a]</sup>	5 <sup>[a]</sup>	2 <sup>[a]</sup>	<1 <sup>[a]</sup>
3	✓	—	✓	3	1	9	<1
4	✓	✓	—	21	6	21	6
5	—	✓	—	2	<1	2	<1

acr = acridine. [a] 45 °C, 24 h.

The solvent for ammonia synthesis was next evaluated with <sup>i</sup>PrOH initially selected due to the known effect of hydrogen bonding networks as an established means to improve proton movement in ground-state PCET processes.<sup>3b</sup> As reported in Table 1 (entry 1), the reaction between **2** and catalytic amounts of **1a** under irradiation with visible blue light with acrH<sub>2</sub> in <sup>i</sup>PrOH produced ammonia in 80 % yield based on **2**. It is likely that the coordinating solvent displaces ammonia in the coordination sphere of the formed manganese(II)-ammonia product, leading to the observation of a high ammonia yield without CO or TMEDA treatment of the non-volatile products. A similar effect has been observed for the light driven multi-site PCET approach in ammonia formation from **2**.<sup>5</sup>

Control experiments (Table 1, entry 2-5) established that all components (light, acrH<sub>2</sub> and photocatalyst **1a**) are

essential to efficiently promote the formation of ammonia from **2** utilizing **1a** as photocatalyst, supporting a photoinduced PCET process. The  $^{15}\text{N}$  isotopologue of **2** was prepared and  $^{15}\text{NH}_3$  was produced in 82 % yield using the standard conditions, confirming the manganese nitride as the nitrogen source in the ammonia observed from the reaction.

To determine whether the ammonia synthesis reaction occurs by direct hydrogen atom transfer (HAT) from the remote N-H bond in **1a** following photoexcitation or by an excited state PCET reaction involving  $\text{acrH}_2$  or  $i\text{PrOH}$  as proton source, the methylated variant, **1b** was explored. The spectroscopic and photophysical properties of **1b** were determined to establish the viability of the complex as a competent photocatalyst. The UV-vis spectrum of **1b** was recorded in THF (40  $\mu\text{M}$ , 298 K) and exhibits similar features to **1a** with two overlapping bands at 435 and 470 nm in the visible region. Excitation of **1b** with 460 nm light resulted in bright luminescence at 634 nm (**1a**: 625 nm).<sup>8b</sup> Along with the ground-state redox potential of  $E_{1/2}^{\text{ox}}(\mathbf{1b}) = 0.56 \text{ V}$  (vs.  $\text{Fc}/\text{Fc}^+$  in THF) the excited state redox potential of **1b** was estimated as  $E_{1/2}^{\text{ox}}(\mathbf{1b})^* = E_{1/2}^{\text{ox}}(\mathbf{1b}) - \Delta E(^3\text{MLCT}) = -1.40 \text{ V}$ . Accordingly, the excited state redox potential of **1b** is comparable to **1a** ( $E_{1/2}^{\text{ox}}(\mathbf{1a})^* = -1.48 \text{ V}$ )<sup>8b</sup> but more reducing than the excited state of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $E_{1/2}^{\text{ox}} = -1.19 \text{ V}$ ,  $\text{bpy} = 2,2'$ -bipyridine).<sup>15</sup> The lifetime of the electronic excited state of **1b** was measured using a time-correlated single photon counting (TCSPC) experiment and produced a value of 99 ns, in good agreement with the data from transient absorption measurements ( $\tau = 109 \text{ ns}$ ).

The similar spectroscopic and photophysical data between **1a** and **1b** establish the latter is an appropriate control for the ruthenium photocatalyst. Subjecting **1b** to the standard reaction conditions with the manganese nitride **2** produced ammonia in a similar yield with  $i\text{PrOH}$  as the solvent and using  $\text{acrH}_2$  as stoichiometric proton and electron source (72 %, Table 1, entry 1). As with **1a**, control experiments with **1b** demonstrate that all components are necessary for the photocatalytic formation of ammonia by **1b** (Table 1, entry 2-5). These results support a pathway whereby ammonia is not formed by direct HAT from the remote N-H functionality in **1a** but rather through the ruthenium acting as an excited state electron transfer catalyst. This mechanistic insight enabled further optimization of the system. It is important to note that a significant background reaction occurs in the absence of any ruthenium photocatalyst - 21% yield of ammonia was obtained upon irradiation of **2** in the presence of  $\text{acrH}_2$  in  $i\text{PrOH}$  solvent. It is possible that a photoexcited state of **2** is responsible for promoting the observed N-H bond-forming reactions. Because ammonia formation from **2** with **1a,b** as photocatalyst does not occur by direct HAT it seems to be plausible to suppress this background reaction by performing the catalytic reaction in an aprotic solvent. Irradiation of a THF solution of **2**,  $\text{acrH}_2$  and catalytic amounts of **1a** or **1b** with visible blue light maintained reasonable ammonia yields (62 %, 80 %, respectively, Table 1, entry 1), while the background reaction without photocatalyst was significantly suppressed (6 % ammonia yield, Table 1, entry 4). The background reaction is likely a result of the

excited state chemistry of **2**, a phenomenon observed previously<sup>5</sup> and currently under investigation.

To obtain additional mechanistic insights for the photocatalytic formation of ammonia from **2** in the presence of either **1a** or **1b**, steady-state and time-resolved Stern-Volmer luminescence quenching experiments were performed in THF. While the diagnostic luminescence of **1a** and **1b** was quenched by the substrate **2**, it was not significantly influenced by excess  $\text{acrH}_2$ . These results suggest that the mode of operation of **1a** and **1b** differs from the pathway of the multi-site PCET approach using homoleptic ruthenium(II) photocatalysts which were shown to be initially reduced to ruthenium(I) by  $\text{acrH}_2$  prior to N-H bond forming steps.<sup>5</sup> It is therefore more likely that **1a** and **1b** act as photoreductants ( $E_{1/2}^{\text{ox}}(\mathbf{1a})^* = -1.48 \text{ V}$ ,  $E_{1/2}^{\text{ox}}(\mathbf{1b})^* = -1.40 \text{ V}$ )<sup>8b</sup> for the manganese nitride **2** ( $E_{1/2}^{\text{red}}(\mathbf{2}) \approx -0.85 \text{ V}$ )<sup>16</sup> in THF, operating in a ruthenium(II)/(III) cycle rather than a ruthenium(I)/(II) cycle. The excited state lifetime of **1a,b** was unaffected by the addition of **2** (Figures S15, S16 and S17),<sup>11</sup> suggesting that **2** quenches the excited state of **1a,b** most likely in a static fashion.<sup>17</sup> Interestingly, the excited state lifetime of **1a** in THF solution was substantially longer (742 ns) than in protic solvent (140 ns in  $\text{MeCN}/\text{H}_2\text{O}$ )<sup>8b</sup> as determined by TCSPC. Most likely, proton exchange with protic solvent serve as an extra non-radiative decay channel for the electronic excited state of **1a**.<sup>18</sup>

The nature of the manganese product following photocatalytic ammonia formation from **2** was also studied. Analysis of the non-volatile residue after the reaction by X-band electron paramagnetic resonance (EPR) spectroscopy in benzene solution at room temperature showed an extremely broad signal centred around  $g = 2.0$ , consistent with previously reported related high-spin manganese(II) complexes.<sup>19</sup> Due to the extreme broadening of the signal, attempts were made to independently synthesize **3** for comparison. Treatment of  $\text{MnCl}_2$  with a stoichiometric amount of the dilithiated ligand quantitatively produced **3** (Scheme S2). By the comparison of the X-band EPR spectrum of **3** in benzene with the spectrum of the non-volatile residue of the photocatalytic reaction (Figure S21),<sup>11</sup> the formation of **3** as the manganese product was established. The high sensitivity of **3** prohibited its characterization by mass spectrometry or single crystal X-ray diffraction. To further prove the nature of **3** it was converted in high yield to the manganese nitride **2**.<sup>11</sup>

## Conclusions

In summary, a concept for the formation of weak N-H bonds relevant to ammonia synthesis was explored. In addition to the established ground-state phenomenon of coordination induced bond weakening, extension of this concept to excited state N-H BDFEs was explored. While ruthenium complexes with remote N-H bonds were effective for photoinduced ammonia synthesis from the manganese nitride **2**, control experiments support a pathway where these complexes act as photoreductants rather than HAT agents in THF. Nevertheless, ammonia yields up to 80 % were observed using **1a** and **1b** as photocatalysts. Luminescence quenching

experiments support that **1a** and **1b** operate in a ruthenium(II)/(III) cycle rather than a ruthenium(I)/(II) alternative. Because of static luminescence quenching, it is likely that electron and proton transfer occur at different sites resulting in a stepwise excited state PCET pathway where the hydrogens for the ammonia are provided by the terminal proton and electron source,  $\text{acrH}_2$ , because *N*-methylation in **1b** neither influences the reactivity nor the mechanism of the presented photocatalytic systems based on **1a,b**.

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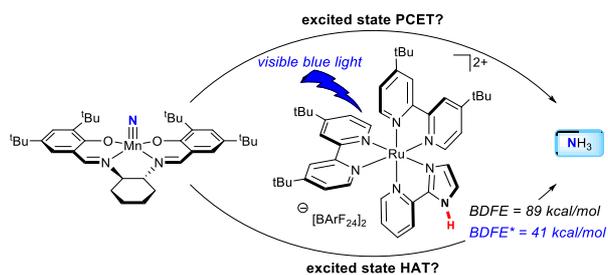
## Conflicts of interest

There are no conflicts to declare.

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## Table of Contents



Development of concepts to form weak N-H bonds is crucial for understanding and improving ammonia formation with homogeneous metal catalysts. Using heteroleptic ruthenium(II) complexes to harvest visible blue light by excited state bond-weakening and their application as photocatalyst leads to the formation of ammonia from a manganese nitride. Mechanistic insights were gained from synthetic ligand modification and luminescence quenching experiments.

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