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# Room-temperature H<sub>2</sub> splitting and N<sub>2</sub>-hydrogenation induced by a neutral Lu<sup>II</sup> complex

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## Abstract

The direct splitting of the H<sub>2</sub> and N<sub>2</sub> molecules are challenging reactions that are closely related to the Haber–Bosch ammonia synthesis process. Until now, such reactivity has never been observed in the case of molecular lanthanide species. Here, we show that careful selection of the ligand scaffold allows the isolation and characterization of a kinetically stable but highly reactive Lu<sup>II</sup> complex. This divalent lanthanide species enables direct H<sub>2</sub> splitting at room temperature, an unknown reactivity in lanthanide chemistry, which has been fully corroborated by DFT calculations. In addition, the Lu<sup>II</sup> complex readily binds N<sub>2</sub>, leading to an end-on coordinated diazenido (N<sub>2</sub>)<sup>2-</sup> lanthanide complex. The latter can be hydrogenated under very smooth conditions (*ca.* 1.2 bar H<sub>2</sub>, ambient temperature) to form a unique Lu<sup>III</sup>–NH<sub>2</sub> complex. Direct N<sub>2</sub> hydrogenation and cleavage are thus accessible using low-valent molecular rare-earth metal complexes.

## Introduction

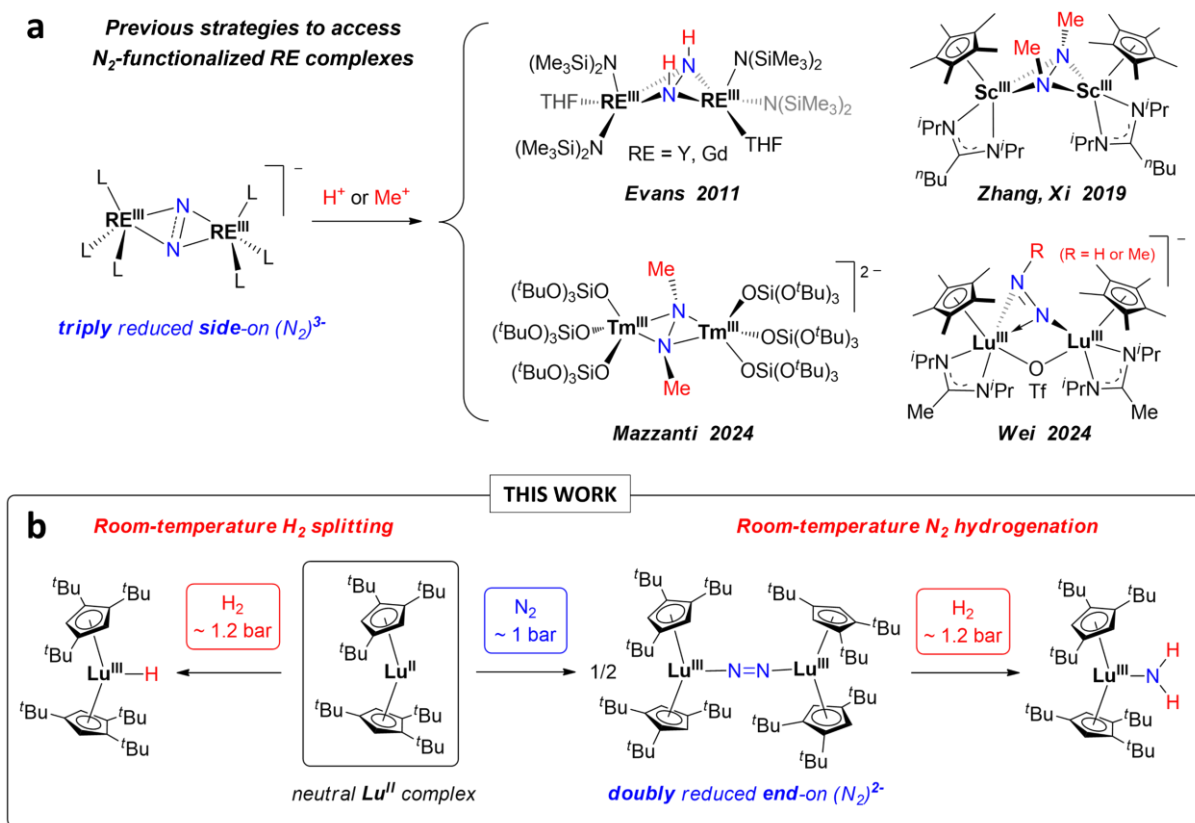
The question of dihydrogen, how it is produced, and how it is used is central to sustainability issues and the decarbonization of the industry.<sup>1</sup> The reversibility of catalytic hydrogenation and dehydrogenation processes is at the heart of this question, as is the transport of H<sub>2</sub> by liquid organic carriers (LOHC).<sup>2</sup> This is particularly true in research on Sustainable Aviation Fuels (SAF) and shipping. Ammonia has been proposed as a desirable hydrogen carrier for the latter because of its hydrogen density and also as a direct fuel.<sup>3</sup> Still, direct ammonia combustion poses the question of N<sub>2</sub>O formation, a potent greenhouse gas.<sup>4</sup> Catalytic processes that combine the cleavage of H<sub>2</sub> and selective transfer to nitrogen are desirable. Using low-cost heterogeneous catalytic systems, the Haber–Bosch process is currently the most efficient industrial process for producing ammonia by nitrogen hydrogenation.<sup>5</sup>

While it is difficult to question the massive production of ammonia *via* this process, smaller-scale units in less industrial environments, where H<sub>2</sub> is produced from green methods, could make way for catalysts capable of generating ammonia at lower energy costs and with greater versatility.<sup>3</sup> Developing processes that can split the H<sub>2</sub> molecule and selectively functionalize simple substrates, such as nitrogen (for ammonia)<sup>6</sup> or CO<sub>2</sub> (for formic acid or methanol),<sup>7</sup> remains a major challenge in modern organometallic chemistry.

Homogeneous pathways for converting N<sub>2</sub> to NH<sub>3</sub> have been made recently, principally with transition metals and uranium.<sup>8</sup> From a mechanistic point of view, the conversion of N<sub>2</sub> and H<sub>2</sub> to ammonia involves different possible scenarios. In the first one, H<sub>2</sub> cleavage occurs first, forming hydride species, which then transfer the hydrogen atoms to dinitrogen. In the second one, N<sub>2</sub> cleavage occurs first, and the resulting nitride is hydrogenated. In the last scenario, synergetic hydrogenation of a reduced N<sub>2</sub> ligand occurs. Among these possibilities, the role of multi-metallic hydride species in the hydrogen atom transfer to dinitrogen has been documented by Hou and co-workers.<sup>9</sup> Hydrogenation of bridged nitrido units, formed after cleavage of dinitrogen, has been recently reported by the groups of Walter and Zhu.<sup>8d,10</sup> It is noteworthy that the direct hydrogenation of reduced dinitrogen adducts has been only described with an organometallic Zr complex.<sup>6b</sup>

In the case of rare-earth (RE) elements, which are constituted by the lanthanides along with the closely related Y and Sc, very rare examples of N<sub>2</sub> functionalization have been disclosed. Corresponding complexes have been obtained by reaction of complexes bearing side-on triply-reduced (N<sub>2</sub>)<sup>3-</sup> ligands with electrophiles or proton donors (Figure 1a),<sup>11</sup> but direct reaction with H<sub>2</sub> has not been witnessed to date. Recently, Arnold and co-workers showed that dinuclear Sm and Ce complexes could generate bis- and tris(silyl)amine with a turnover of up to 4 using a large excess of metallic reductant in the presence of excess Me<sub>3</sub>SiCl or proton sources.<sup>12</sup> Additionally, following seminal reports on photochemical assistance in producing ammonia from N<sub>2</sub>,<sup>13</sup> the group of Borbas recently reported photocatalytic ammonia formation by a Sm complex bearing a built-in coumarin chromophore.<sup>14</sup> During revision of this article, the group of Peters achieved electrocatalytic N<sub>2</sub> reduction to ammonia using a tandem Sm/Mo catalytic system in the presence of proton sources.<sup>15</sup>

Historically, the chemistry of divalent lanthanide complexes has been dominated by Sm<sup>II</sup>, Eu<sup>II</sup>, and Yb<sup>II</sup> species, which feature relatively stable 4f<sup>n</sup> Ln<sup>II</sup> electronic configurations.<sup>16</sup> The corresponding metallocene chemistry has flourished, especially in the context of single-electron transfer (SET) reductions, typically leading to Ln<sup>III</sup> end products.<sup>17</sup> Although cyclopentadienyl (Cp) complexes of all the lanthanides, except radioactive Pr, have been isolated in the +II oxidation state,<sup>18</sup> fewer studies have focused on the so-called “non-classical divalent lanthanides”,<sup>19</sup> consisting of the remainder of the 4f series. This relative scarcity can be traced back to experimental difficulties in handling these very reactive and reducing species.<sup>20</sup> Among them, Tm<sup>II</sup> is the most accessible in terms of reduction potential, yet displays strong reducing properties beneficial for molecular activation *via* SET reactions.<sup>11d,21</sup>

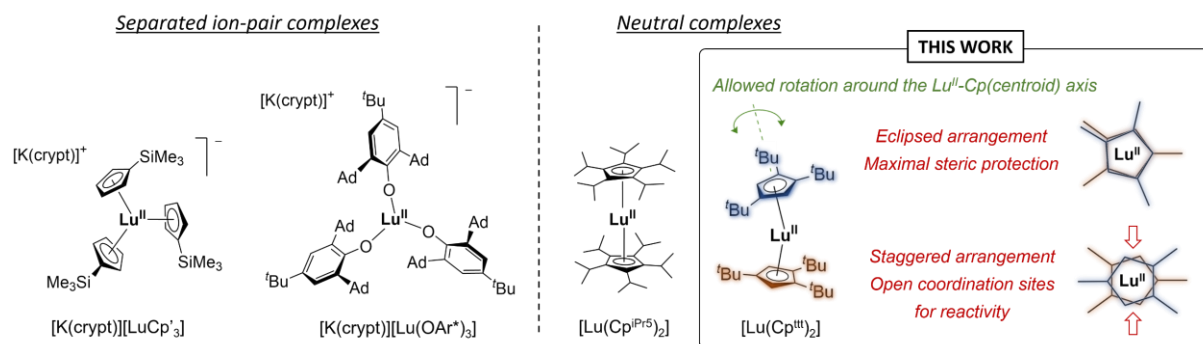


**Figure 1.** (a) Previous strategies to access  $N_2$ -functionalized rare-earth metal complexes. (b) Reactivity described in this work.

In this context, our group recently showed that the  $Tm^{II}$  complex  $[Tm(Cp^{ttt})_2]$  ( $Cp^{ttt}$  = 1,2,4-tris(*tert*-butyl)cyclopentadienyl) displays unique reactivity in terms of CO reductive coupling and subsequent functionalization reactions.<sup>22</sup> The choice of the  $Cp^{ttt}$  ligand was crucial to kinetically stabilize the reactive metal center while still allowing the coordination of an exogenous ligand.<sup>23</sup> The three bulky *tert*-butyl substituents confer high thermal stability but slightly hamper reactivity, as  $[Tm(Cp^{ttt})_2]$  does not react with  $N_2$ , contrary to the less sterically protected analogues.<sup>21a,24</sup> An extreme case of stabilization was recently reported by Long, Harvey and co-workers through the use of the penta-substituted  $Cp^{iPr5}$  ( $Cp^{iPr5}$  = penta-isopropylcyclopentadienyl) ligand. The redox potential of the corresponding  $Tm^{II}$  complex was evaluated as high as  $-1.57$  V, more than 1 V less reducing than other  $Tm^{II}$  Cp-type complexes.<sup>20,22</sup>

In the present study, we were interested in investigating whether the  $Cp^{ttt}$  ligand would allow the stabilization of even more reducing  $Lu^{II}$  complexes. In addition to advantageous properties in terms of quantum applications,<sup>25</sup>  $Lu^{II}$  species appear particularly attractive to uncover novel reactivities, especially in terms of small molecule activation *via* SET reductions. Unlike  $Tm^{III}$  species that are strongly paramagnetic,  $Lu^{III}$  end products are diamagnetic, allowing precise monitoring of reactions by multinuclear NMR spectroscopy. Surprisingly, only three molecular  $Lu^{II}$  complexes have been reported to date (Figure 2), the two separated ion-pair complexes  $[K(crypt)][LuCp'_3]$  ( $Cp' = C_5H_4SiMe_3$ )<sup>26</sup> and

[K(crypt)][Lu(OAr\*)<sub>3</sub>] (OAr\* = 2,6-bis(adamantly)-4-<sup>t</sup>Bu-C<sub>6</sub>H<sub>2</sub>O),<sup>25,27</sup> and the neutral [Lu(Cp<sup>iPr5</sup>)<sub>2</sub>] complex.<sup>18d</sup>



**Figure 2.** Structures of the previously reported Lu<sup>II</sup> complexes and comparison with this work. The fluxional behavior of the Cp<sup>ttt</sup> ligand allows the formation of two possible arrangements: the eclipsed arrangement offers maximal steric protection for the metal center and enhanced kinetic stability while the staggered arrangement provides available coordination sites for SET reactivity.

In this work, we show how the fluxional behavior of the Cp<sup>ttt</sup> ligand in [Lu(Cp<sup>ttt</sup>)<sub>2</sub>] allows the stabilization of a highly reactive Lu<sup>II</sup> complex while still offering an open coordination site for original reactivity (Figure 2). It is worth noting that, during this work, Evans and co-workers reported the synthesis of the related [Sc(Cp<sup>ttt</sup>)<sub>2</sub>] and its coordination chemistry towards CO and isocyanides.<sup>28</sup> Herein, we show that [Lu(Cp<sup>ttt</sup>)<sub>2</sub>] induces unprecedented reactivities in lanthanide chemistry, such as direct H<sub>2</sub> splitting and N<sub>2</sub> hydrogenation under very smooth conditions (Figure 1b).

## Results and discussion

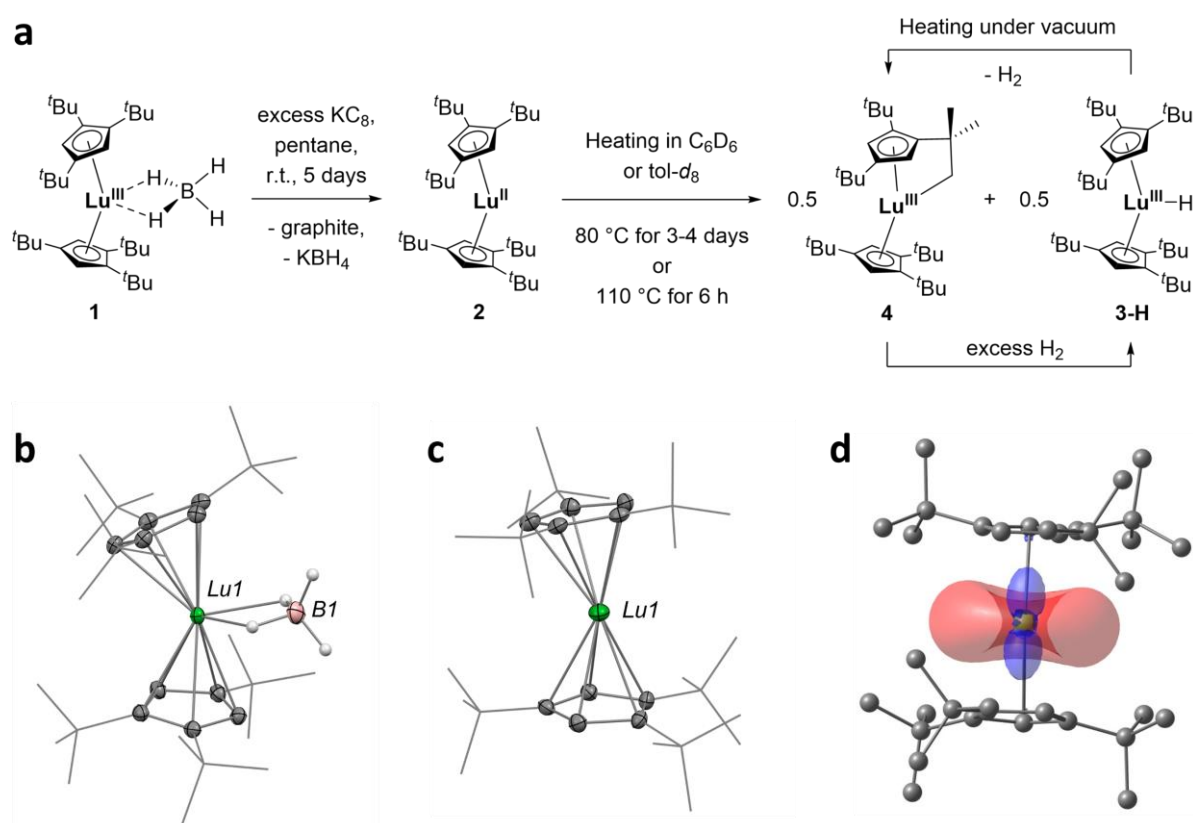
### Synthesis and characterization of [Lu(Cp<sup>ttt</sup>)<sub>2</sub>]

The parent Lu<sup>III</sup> complex, [Lu(Cp<sup>ttt</sup>)<sub>2</sub>(BH<sub>4</sub>)] (**1**), was prepared by a salt metathesis reaction between KCp<sup>ttt</sup> and [Lu(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>],<sup>29</sup> using a procedure similar to that described for the synthesis of [Ln(Cp<sup>ttt</sup>)<sub>2</sub>(BH<sub>4</sub>)] (Ln = Tm, Dy),<sup>21c,30</sup> and isolated in a 39% crystalline yield. In contrast to the preparation of other [Ln(Cp<sup>ttt</sup>)<sub>2</sub>(BH<sub>4</sub>)] complexes,<sup>21c,30-31</sup> longer reaction times were necessary to achieve reasonable conversion into **1**. The latter was isolated in a 39% yield upon crystallization from pentane at -40 °C. The mother liquor, which was found to be composed of **1** along with the corresponding half-sandwich complex [Lu(Cp<sup>ttt</sup>)(BH<sub>4</sub>)<sub>2</sub>(THF)],<sup>32</sup> can be conveniently reused in subsequent synthesis batches of **1** to improve the yield. As lutetium is the last member in the 4f series, its ionic radius may explain the increased difficulty in accommodating two bulky Cp<sup>ttt</sup> ligands around the metal center.

The X-ray structure of **1** (Figure 3b) confirmed the coordination of two η<sup>5</sup>-Cp<sup>ttt</sup> and one κ<sup>2</sup>-bound borohydride to the Lu<sup>III</sup> center. In comparison with the isomorphous Tm<sup>III</sup> complex,<sup>21c</sup> the Lu–Cp(ctr) (ctr = ring centroid) separation is slightly shorter (2.322 Å for Lu vs. 2.356 Å for Tm), in agreement with the smaller ionic radius of Lu.<sup>33</sup> The <sup>1</sup>H NMR spectrum of **1** displays three resonances

for the coordinated Cp<sup>ttt</sup> ligands, consistent with an overall  $C_{2v}$  symmetric species in solution. One notable feature in the IR spectrum of **1** is the presence of three moderately intense bands in the region 2000–2500  $\text{cm}^{-1}$ , more precisely one doublet band at 2459 and 2413  $\text{cm}^{-1}$  associated with one additional band at 2112  $\text{cm}^{-1}$ , arising from the terminal  $\kappa^2$ -bound  $\text{BH}_4$ .<sup>34</sup> These bands are blue-shifted by *ca.* 50  $\text{cm}^{-1}$  with respect to those in  $[\text{LuCp}_2(\text{BH}_4)(\text{THF})]$  initially reported by Schumann and co-workers.<sup>35</sup>

To access  $[\text{Lu}(\text{Cp}^{\text{ttt}})_2]$  (**2**), reduction of **1** was performed by treatment with excess  $\text{KC}_8$  in pentane at room temperature under an argon atmosphere for 5 days (Figure 3a). As **2** is extremely sensitive towards  $\text{N}_2$ , special precautions must be taken to avoid adventitious reaction with traces of  $\text{N}_2$ , even when working in an argon-filled glovebox (see Supplementary Information for details). It should be noted that previous reports on the attempted isolation of non-classical divalent lanthanide  $[\text{Ln}(\text{Cp}^{\text{ttt}})_2]$  complexes highlighted the difficulty in isolating these species owing to their high reactivity and solubility.<sup>36</sup>



**Figure 3.** (a) Synthesis and thermolysis reactivity of **2**. (b) Molecular structures of **1** and (c) of one of the two independent molecules of **2** in the solid state (see also Figure S40). The thermal ellipsoids are at the 40% probability level, except for the <sup>t</sup>Bu groups depicted in wireframe, and H atoms have been omitted for clarity, except those on the borohydride unit. (d) SOMO of **2** consisting of the Lu  $d_{2z^2}$  orbital.

Building on our recent success in crystallizing the related Tm<sup>II</sup> complex  $[\text{Tm}(\text{Cp}^{\text{ttt}})_2]$ ,<sup>22</sup> orange-red crystals of **2** suitable for X-ray diffraction (XRD) studies were isolated in 18% yield after

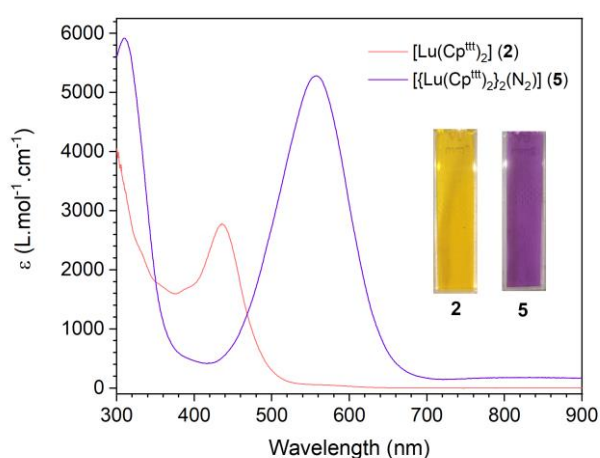
crystallization from pentane at low temperature ( $-40\text{ }^{\circ}\text{C}$ ). Although the isolated crystalline yield is relatively low, which can be traced back to the very high solubility of **2** in hydrocarbon solvents, the mother liquor was found to be composed of **2** along with variable amounts of clean thermolysis products (see below), as evidenced by  $^1\text{H}$  NMR analysis.

The molecular structure of **2** in the solid state (Figure 3c) displays two independent molecules of **2** in the asymmetric unit, featuring very similar metric data, and confirms the formation of a base-free bent metallocene complex. The two  $\text{Cp}^{\text{ttt}}$  ligands are in an eclipsed arrangement, providing efficient kinetic stabilization of the  $\text{Lu}^{\text{II}}$  metal center. A comparison of the steric shielding in **2** vs. that in  $[\text{Lu}(\text{Cp}^{\text{iPr5}})_2]^{18\text{d}}$  by the Guzei method<sup>37</sup> (see Supporting Information for details) revealed very similar  $G$  values (83.5 and 85.5%, respectively). The bent arrangement in **2**, which displays an average  $\text{Cp}(\text{ctr})\text{--Lu--Cp}(\text{ctr})$  ( $\text{ctr}$  = ring centroid) angle of  $167.2^{\circ}$ , is typical for Cp-based  $\text{Ln}^{\text{II}}$  sandwich complexes.<sup>17</sup> Linear coordination has only been observed when using the  $\text{Cp}^{\text{iPr5}}$  ligand, which presents a higher symmetry and different steric profile than the  $\text{Cp}^{\text{ttt}}$  ligand.<sup>18\text{d}}</sup> In contrast to the previously reported  $[\text{Ln}(\text{Cp}^{\text{ttt}})_2]$  ( $\text{Ln}$  = Sm, Eu, Yb, Tm) complexes, for which a monotonic contraction in the  $\text{Ln--Cp}(\text{ctr})$  separation of  $ca.$   $0.018\text{ \AA}$  is observed per atomic number increment, the average  $\text{Lu--Cp}(\text{ctr})$  distance of  $2.305\text{ \AA}$  in **2** does not follow this trend (Figure S44). Although there have been discussions regarding the model that should be best used to fit the variation in bond distances due to the lanthanide contraction,<sup>38</sup> the  $\text{Lu--Cp}(\text{ctr})$  in **2** appears  $ca.$   $0.056\text{ \AA}$  shorter as would be expected from a simple linear fit. The apparent decrease in ionic radius can be traced back to the  $4f^n5d^1$  ( $n = 14$ ) configuration for  $\text{Lu}^{\text{II}}$ , compared to the  $4f^{n+1}$  configuration adopted by the divalent Sm, Eu, Yb and Tm congeners, and covalent interactions involving the populated 5d orbital.<sup>26,39</sup>

The  $^1\text{H}$  NMR spectrum of **2** at room temperature displays two hardly identifiable broad resonances, which may be assigned to the fluxionality of the  $\text{Cp}^{\text{ttt}}$  ligands. Upon heating to  $80\text{ }^{\circ}\text{C}$ , a better-resolved spectrum can be obtained with two main resonances at  $\delta$  2.0 ( $\Delta\nu_{1/2} \approx 70\text{ Hz}$ ) and 0.9 ppm ( $\Delta\nu_{1/2} \approx 200\text{ Hz}$ ) in a respective 1:2 ratio, corresponding to the  $^t\text{Bu}$  groups of freely rotating  $\text{Cp}^{\text{ttt}}$  rings.<sup>40</sup> Determination of the solution magnetic moment of **2** by the Evans' NMR method<sup>41</sup> led to a value of  $1.5\ \mu_{\text{B}}$ , which agrees relatively well with that of  $1.7\ \mu_{\text{B}}$  expected for one unpaired electron in a d shell. The experiment value should yet be regarded as a lower limit given the high sensitivity and reactivity of **2**. Continuous-wave X-band EPR measurements performed on a solution of **2** in pentane at room temperature only revealed one broad isotropic signal at  $g = 2.274$  with unresolved hyperfine coupling, which disappeared upon addition of  $\text{N}_2$  (Figures S37–38). Recording the EPR spectrum of **2** at lower temperature ( $105\text{ K}$ ) in a frozen pentane solution did not result in a better resolved spectrum. In contrast, an eight-line EPR pattern was reported for  $[\text{K}(\text{crypt})][\text{LuCp}^{\text{t}}_3]$  ( $^{175}\text{Lu}$ ,  $I = 7/2$ , 97.4% natural abundance),<sup>26</sup> whereas  $[\text{Lu}(\text{Cp}^{\text{iPr5}})_2]$  did not give rise to an observable signal.<sup>18\text{d}}</sup> The geometry of complex **2** was optimized at the DFT level (B3W91 functional) and the optimized geometry compares well with the experimental one. In particular, the  $\text{Lu--Cp}(\text{ctr})$  distance is well reproduced ( $2.335$  vs.  $2.305\text{ \AA}$  experimentally) as well as the  $\text{Cp}(\text{ctr})\text{--Lu--Cp}(\text{ctr})$  angle ( $166.6^{\circ}$  vs.  $167.2^{\circ}$  experimentally). The

SOMO (Figure 3d) of **2** appears to be the metal  $d_{z^2}$  orbital, in line with a  $\text{Lu}^{\text{II}} 4f^{14}5d^1$  configuration, and agrees with the isotropic  $g$  value of the EPR signal.

The UV–vis spectrum of **2** in pentane (Figure 4) shows a major absorption band at 435 nm ( $\epsilon = 2800 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), along with the onset of a strong band below 350 nm. It contrasts with the spectrum of the related neutral  $[\text{Lu}(\text{Cp}^{\text{iPr5}})_2]$  complex, which features minimal absorption in the visible region.<sup>18d</sup> In comparison, in the  $[\text{K}(\text{crypt})][\text{LuCp}'_3]$  separated ion-pair complex, an intense band was observed at 518 nm and assigned to a metal–to–ligand charge-transfer (MLCT) transition.<sup>26</sup> TDDFT calculations were carried out in *n*-pentane to obtain the UV–vis spectrum of **2** (Figure S45). An absorption band is found around 400 nm, in agreement with the experimental spectrum, and consists of an MLCT excitation from the SOMO ( $d_{z^2}$ ) to the  $\text{Lu}\text{--}\text{Cp}^{\text{III}}$  antibonding orbital.



**Figure 4.** Room temperature UV–vis–NIR absorption spectra in pentane of **2** ( $C = 4.5 \text{ mM}$ ) and *in situ* formed **5** ( $C = 0.8 \text{ mM}$ ) and photograph of the cuvettes.

### Thermolysis reactivity of **2**

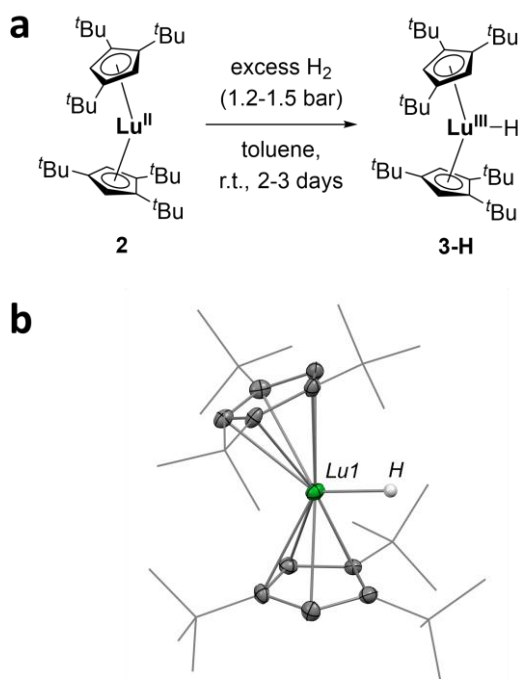
The thermal stability of **2** was investigated at different concentrations by  $^1\text{H}$  NMR and UV–vis spectroscopy. For a dilute solution of **2** in pentane ( $C = 4.5 \text{ mM}$ ), a decrease in intensity of *ca.* 6% was observed in the UV-vis spectrum for the most intense absorption band at 435 nm over 2 h (Figure S35). More concentrated solutions were found to be more stable over time as the  $^1\text{H}$  NMR spectrum of **2** in  $\text{C}_6\text{D}_6$  ( $C = 30\text{--}50 \text{ mM}$ ) revealed no significant formation of thermolysis products over several days. The thermal stability of  $\text{Lu}^{\text{II}}$  complexes appears to be highly dependent on the ligand environment: at room temperature and in hydrocarbon solvents,  $[\text{K}(\text{crypt})][\text{LuCp}'_3]$  features a half-life of *ca.* 20 min,<sup>26</sup> whereas  $[\text{K}(\text{crypt})][\text{Lu}(\text{OAr}^*)_3]$  slowly decomposes over the course of several days.<sup>25,27</sup> An exceptional thermal stability was reported for  $[\text{Lu}(\text{Cp}^{\text{iPr5}})_2]$ , synthesized upon extensive heating at elevated temperatures ( $160\text{--}180 \text{ }^\circ\text{C}$ ).<sup>18d</sup>

Heating a solution of **2** in  $\text{C}_6\text{D}_6$  at  $80 \text{ }^\circ\text{C}$  for several days led to an unexpectedly clean and well-defined  $^1\text{H}$  NMR spectrum, showing the formation of the  $\text{Lu}^{\text{III}}$  hydride complex **3-H** and the cyclometallated complex **4** (Figure 3a) in close to equimolar amounts (see Figures S11–13). The identity

of **4** was testified by its reactivity towards hydrogenolysis, as complete and immediate conversion into **3-H** occurred upon addition of H<sub>2</sub> (Figure S12). A similar hydrogenolysis reactivity had been earlier reported by Andersen and co-workers on the cerium analogue of **4**.<sup>42</sup> The <sup>1</sup>H NMR spectrum of **4** displays, notably, two doublets at  $\delta$  0.65 and  $-0.18$  ppm, with a <sup>2</sup>J<sub>HH</sub> coupling constant of 13.5 Hz, for the diastereotopic protons of the cyclometallated methylene group. The characterization data of **3-H** will be discussed in detail in the next section. The hydrogenolysis reaction is reversible as heating a degassed solution of **3-H** under static vacuum for several days led to complete conversion back to **4** (Figures S14–15). The formation of **4** and its reactivity with H<sub>2</sub> to form **3-H** were also investigated computationally. The formation of **4** implies a bimetallic transition state (TS) on the triplet spin potential energy surface (PES) where the hydrogen from one <sup>t</sup>Bu group of one molecule of **2** is transferred to the Lu center of a second molecule of **2** (Figure S46). The associated barrier is 39.0 kcal·mol<sup>-1</sup>, in line with the relative stability of **2** at room temperature and the experimental observation of a slow thermal degradation at 80 °C. Yet, the reaction is exothermic by 20.8 kcal·mol<sup>-1</sup> due to the formation of one equivalent of **4** and one of **3-H**. The hydrogenolysis of complex **4** to form **3-H** (Figure S47) is both kinetically (barrier of 7.2 kcal·mol<sup>-1</sup>) and thermodynamically favorable ( $-15.8$  kcal·mol<sup>-1</sup>). The activation barrier of 22.9 kcal·mol<sup>-1</sup> for the reverse transformation is fully consistent with the dehydrogenation of **3-H** into **4** accessible upon heating.

#### Reactivity of **2** towards small molecules: H<sub>2</sub> splitting

The clean access to **2** as a rare base-free, room-temperature stable and highly soluble divalent lanthanide complex gave us the opportunity to study its reactivity towards industrially relevant small molecules, such as H<sub>2</sub>, which usually does not bind strongly with f-elements. Herein, its coordination to the lanthanide center in **2** would not suffer from the presence of a better ligand.<sup>43</sup> Due to its unique properties, **2** reacts with H<sub>2</sub> under very smooth conditions (1.2–1.5 bar of H<sub>2</sub>, ambient temperature), leading to quantitative conversion into the hydride complex **3-H** over the course of 1–3 days (Figure 5a). Reaction with D<sub>2</sub> proceeded similarly, yielding the Lu<sup>III</sup> deuteride **3-D**, without any appreciable deuteration of the ligand backbone.<sup>42</sup> It should be stressed that the reactivity of **2** with H<sub>2</sub> is much faster than its thermal decomposition into **3-H** and **4** (see Figure S35), meaning that another direct pathway must be active to form **3-H** (see below for mechanistic insights by DFT calculations).



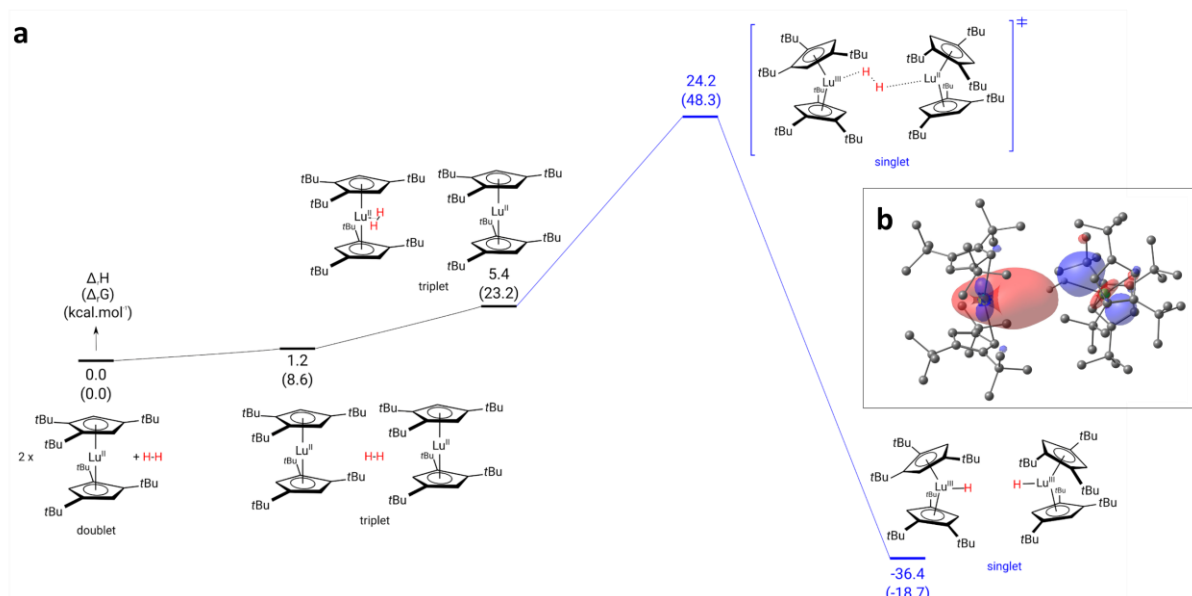
**Figure 5.** (a) Synthesis of **3-H** by reaction of **2** with H<sub>2</sub>. (b) Molecular structure of **3-H** in the solid state with thermal ellipsoids at the 40% probability level (except for the <sup>t</sup>Bu groups depicted in wireframe). H atoms, except for the lutetium H atom, have been omitted for clarity.

In the <sup>1</sup>H NMR spectrum of **3-H**, the hydride resonance is detected as a downfield singlet at  $\delta$  10.33 ppm while the aromatic Cp<sup>ttt</sup> protons give rise to a singlet at  $\delta$  6.13 ppm. Accordingly, a singlet at  $\delta$  10.33 ppm was observed in the <sup>2</sup>H NMR spectrum of **3-D** (Figure S9). Unrestricted rotation of the Cp<sup>ttt</sup> ligands leads to an overall C<sub>2v</sub> symmetry in solution, as evidenced by the presence of two singlets for the <sup>t</sup>Bu groups in a 2:1 ratio.<sup>40a</sup> In the IR spectrum of **3-H**, the Lu–H stretching frequency could not be identified, even upon direct comparison with the spectrum of **3-D**, similarly to what was also reported for the Ce analogue [Ce(Cp<sup>ttt</sup>)<sub>2</sub>H].<sup>42</sup> The molecular structures of **3-H** and **3-D** were unambiguously established by single-crystal XRD analyses, confirming the formation of rare examples of monomeric Ln<sup>III</sup> complexes bearing terminal hydride or deuteride ligands (Figure 5b and Figure S42).<sup>44</sup> Although the H and D atoms on lutetium were located on the electron density map, the Lu–H/D separations (1.73(8) and 1.81(5) Å, respectively) suffer from low precision and may not be fully representative of the actual bond distances. They appear particularly short compared to the lutetium-hydride distances in related Cp-type complexes.<sup>45</sup> The Lu–Cp(ctr) distances in **3-H/D** are identical, within experimental error, to those in **2**, whereas the presence of the hydride leads to a more acute Cp(ctr)–Lu–Cp(ctr) angle (in average 167.2° in **2** vs. 153.1° in **3-H**), *i.e.* a larger deviation from linearity.

To the best of our knowledge, direct H<sub>2</sub> splitting by molecular lanthanide complexes is unprecedented to date. This strategy offers a novel route for the synthesis of molecular Ln<sup>III</sup>–H species, typically obtained by hydrogenolysis of Ln–alkyl bonds.<sup>34b,44,46</sup> It can be noted that, in rare instances, molecular RE hydrides have been obtained upon treatment of trivalent complexes with strong alkali

metal reductants.<sup>45a,47</sup> However, such reactions did not involve H<sub>2</sub> activation but rather undefined hydrogen abstraction from solvents or possible aromatic C–H activation.<sup>47e</sup> Although elemental zerovalent lanthanides are known to react with hydrogen at elevated temperatures to afford binary Ln hydrides, no such reaction has been observed with molecular Ln species.<sup>34b,44</sup> Weak coordination of H<sub>2</sub> to a lanthanide complex has only been spectroscopically evidenced for the base-free Eu<sup>II</sup> complex [Eu(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>], in which case no metal oxidation and formation of a hydride complex occurred.<sup>48</sup> Very recently, this phenomenon has been extended to 5f elements with spectroscopic and computational evidence of the reversible formation of a U<sup>III</sup>–H<sub>2</sub> complex.<sup>49</sup> Regarding heterogeneous lanthanide systems, nondissociative dihydrogen binding has also been very recently evidenced by solid-state NMR studies under pressure of H<sub>2</sub>.<sup>50</sup> Finally, it is worth noting that, within the actinide series, some U<sup>II</sup> and Th<sup>II</sup> complexes were reported to activate H<sub>2</sub>, leading to higher-valent hydride complexes, but the corresponding mechanisms remain elusive.<sup>51</sup> The observed H<sub>2</sub> splitting reactivity of **2** contrasts with the reported H<sub>2</sub> elimination reactivity of the mixed-valent ytterbium hydride complex [{Yb(Cp\*)<sub>2</sub>(μ-H)}].<sup>52</sup> This reverse pathway may be linked to the greater thermodynamic stability of Yb<sup>II</sup> compared to Lu<sup>II</sup>.

DFT calculations were performed to shed light on the mechanism of the unusual H<sub>2</sub> activation reactivity of **2**. Reaction profiles were calculated on the triplet and singlet Potential Energy Surface (PES) (Figure S48), and the most probable profile is discussed (Figure 6a). The reaction begins with the formation of a weak van der Waals adduct of H<sub>2</sub> in between two molecules of **2** (1.2 kcal·mol<sup>-1</sup>). This adduct yields to the side-on coordination of H<sub>2</sub> to one Lu<sup>II</sup> center while the second Lu<sup>II</sup> remains in the vicinity (+5.4 kcal·mol<sup>-1</sup>). It is important to note that these two adducts do not imply oxidation of the Lu center since the most stable one is on the triplet PES and the unpaired spin density is mainly located at the two Lu centers (see Figure S49). However, the H–H distance (0.82 Å) is elongated, and the SOMO implies interaction between a d orbital on Lu<sup>II</sup> and the σ\* of H<sub>2</sub> (see Figure S50). This coordination has thus decreased the energy of the H<sub>2</sub> σ\* orbital (which is now involved in the SOMO), allowing further reduction of H<sub>2</sub> *via* a bimetallic transition state (TS). At the TS, H<sub>2</sub> is undergoing a two-electron reduction that allows the disruption of the H–H bond with an accessible barrier of 24.2 kcal·mol<sup>-1</sup>. The value for this activation barrier is fully consistent with the relatively slow reaction observed at room temperature. The TS was located on the singlet PES in line with a two-electron reduction and the need of bimetallic activation since each Lu<sup>II</sup> is only able to do one single electron transfer. The H<sub>2</sub> molecule is becoming end-on coordinated to the Lu center (Lu–H distance of 2.20 Å) while the H–H distance is only marginally elongated with respect to the adduct (0.88 Å). The second H···Lu distance remains long (3.47 Å) but the interaction is effective, as highlighted by the HOMO at the TS (Figure 6b), where the two d<sub>z<sup>2</sup></sub> orbitals located on the two Lu atoms overlap with the H<sub>2</sub> σ\* orbital. Following the intrinsic reaction coordinate (IRC), it yields two Lu<sup>III</sup>–H complexes whose formation is highly favorable (–36.4 kcal·mol<sup>-1</sup> with respect to the entrance channel).



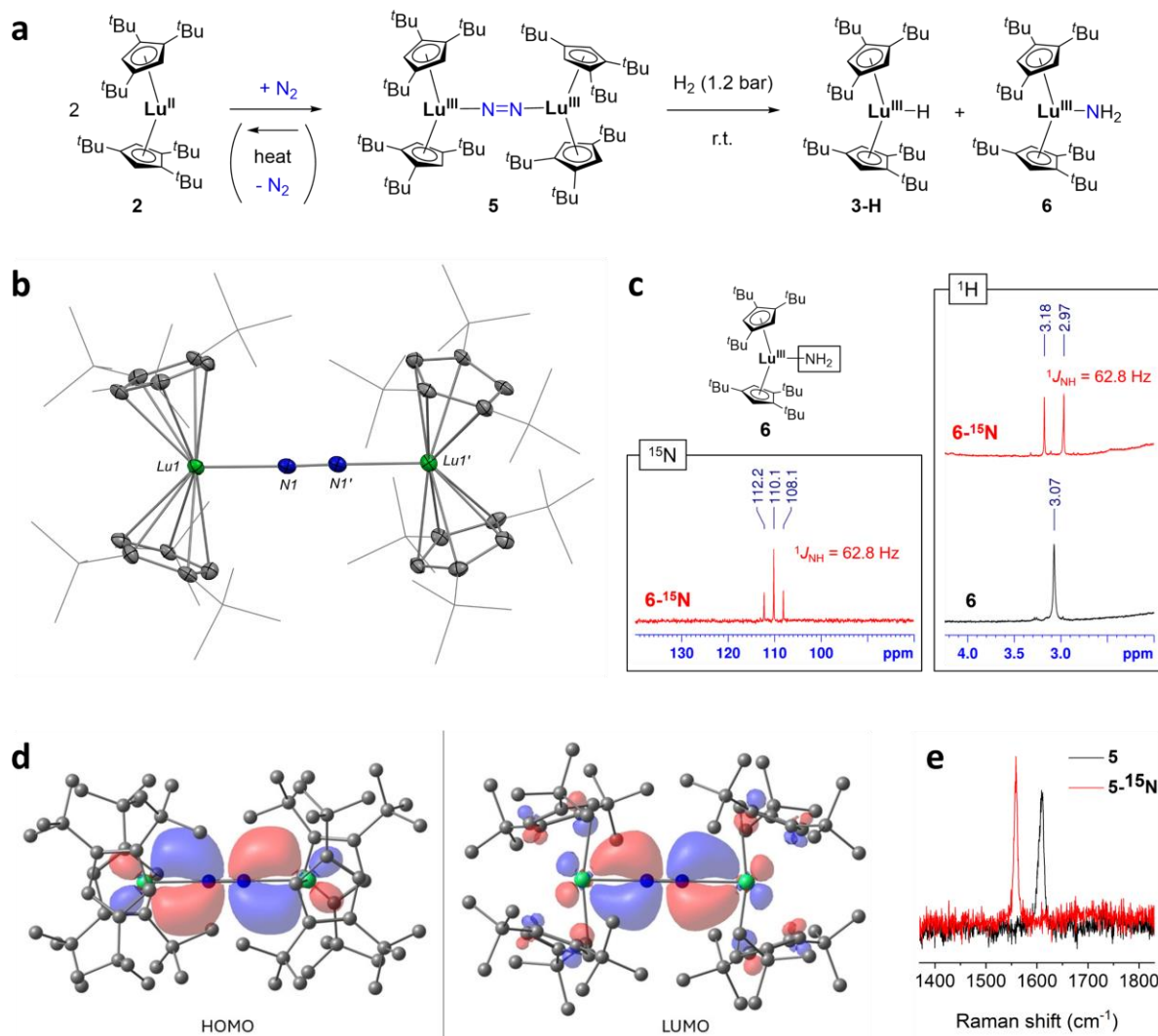
**Figure 6.** (a) Computed energy profile for the reaction of **2** with H<sub>2</sub> leading to the formation of **3-H**. (b) Calculated HOMO at the TS of the reaction between **2** and H<sub>2</sub> showing the two metal d<sub>2</sub> orbitals of two molecules of **2** overlapping with the H<sub>2</sub> σ\* orbital.

### Reactivity of **2** towards small molecules: N<sub>2</sub> coordination

The exceptional sensitivity of **2** towards N<sub>2</sub> prompted us to examine the nature of the resulting product and study the possibility of synergistic H<sub>2</sub>/N<sub>2</sub> activation reactions. The addition of N<sub>2</sub> to a pentane solution of **2** led to the immediate formation of a deep purple suspension of [{Lu(Cp<sup>ttt</sup>)<sub>2</sub>}<sub>2</sub>(μ-η<sup>1</sup>:η<sup>1</sup>-N<sub>2</sub>)] (**5**) (Figure 7a). This work parallels the recent synthesis by Layfield and co-workers of the analogous Gd, Tb, and Dy complexes by *in situ* reaction of the elusive divalent complexes with N<sub>2</sub>.<sup>36b</sup>

Crystals of **5** suitable of X-ray diffraction studies revealed the formation of a centrosymmetric dinuclear Lu<sup>III</sup> complex featuring an end-on bridging (N<sub>2</sub>)<sup>2-</sup> ligand (Figure 7b). Although N<sub>2</sub> coordination on low-valent RE complexes is relatively common, the end-on μ-η<sup>1</sup>:η<sup>1</sup>-N<sub>2</sub> coordination mode is still rare,<sup>36b,53</sup> typically favored by bulky ligands and RE metals of small ionic radii. As expected from the lanthanide contraction, the Lu–N separation of 2.184(5) Å is slightly shorter than the Ln–N separations of 2.325(4), 2.296(4) and 2.268(7) Å in the Gd, Tb and Dy analogues, respectively.<sup>36b</sup> The N–N separation of 1.203(11) Å is consistent with a doubly reduced (N<sub>2</sub>)<sup>2-</sup> ligand, which is corroborated by vibrational spectroscopy. Although the IR spectrum of **5** is very similar to that of **2** (Figure S32) because the N=N vibration is not IR active in this centrosymmetric structure, the Raman spectrum of **5** revealed a sharp band at 1610 cm<sup>-1</sup> for the symmetric N<sub>2</sub> stretch (Figure 7e). This assignment was confirmed by the shift of this signal to 1559 cm<sup>-1</sup> for the <sup>15</sup>N-labeled complex **5**-<sup>15</sup>N. The experimental ratio of frequencies of 1.033 matches the theoretical value of 1.035 derived from reduced mass considerations. It is worth

noting that the extent of  $N_2$  activation in rare-earth metal diazenido complexes seems to particularly depend on the  $(N_2)^{2-}$  coordination mode. For the most common side-on coordination mode, the  $N_2$  stretch lies in the range  $1371\text{--}1473\text{ cm}^{-1}$ ,<sup>11c,54</sup> whereas the reported  $N_2$  stretching vibration in end-on complexes is at higher energy, ranging from  $1595\text{ to }1660\text{ cm}^{-1}$ .<sup>36b,53</sup>



**Figure 7.** (a) Synthesis and hydrogenation reactivity of **5**. (b) Centrosymmetric molecular structure of **5** in the solid state with the thermal ellipsoids at the 40% probability level (except for the <sup>t</sup>Bu groups depicted in wireframe). H atoms and non-coordinating solvent molecules have been omitted for clarity. (c) Details of the NH<sub>2</sub> regions in the <sup>1</sup>H and <sup>15</sup>N NMR spectra of **6** and **6-<sup>15</sup>N**. (d) Calculated HOMO and LUMO of **5**. (e) Raman spectrum of **5** and comparison with that of **5-<sup>15</sup>N**.

Once formed, **5** is only sparingly soluble in hydrocarbon solvents and readily decomposes in ether solvents to unidentified species, which hampered analysis by NMR spectroscopy. The UV-vis spectrum in pentane of *in situ* formed **5** shows the disappearance of the characteristic band of **2** centered at 435 nm, at the expense of two intense absorption bands at 310 ( $\epsilon = 5900\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and 555 nm ( $\epsilon = 5300\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) (Figure 4). The latter band is slightly blue-shifted compared to that

in the corresponding Dy complex, following the preliminary trend observed in the  $[\{\text{Ln}(\text{Cp}^{\text{ttt}})_2\}_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-N}_2)]$  (Ln = Gd, Tb, Dy) series.<sup>36b</sup>

The structure of complex **5** was investigated computationally using the same methodology as before. Both end-on and side-on coordination of  $\text{N}_2$  were considered and the end-on coordination is found to be the most favorable. In the same way, the singlet and triplet spin states were considered for complex **5**, as a recent report by Jones and co-workers demonstrated that the  $(\text{N}_2)^{2-}$  ligand can adopt a triplet ground state by occupying the two formally degenerated  $\pi^*$  orbital of  $\text{N}_2$ .<sup>55</sup> A similar triplet ground state was observed by Evans and co-workers for end-on coordinated dinitrogen Sc and Gd ion-pair complexes supported by silylamide ligands.<sup>53a,53b</sup> In the case of **5**, the singlet is found to be slightly more stable than the triplet by  $1.8 \text{ kcal}\cdot\text{mol}^{-1}$ , consistent with the recent findings of Layfield and co-workers on the Gd, Tb and Dy analogues.<sup>36b</sup> The singlet optimized geometry compares well with the experimental one (Lu–N distance of  $2.20 \text{ \AA}$  and N–N distance of  $1.20 \text{ \AA}$ ), in line with a two-electron reduction of  $\text{N}_2$  upon coordination to two  $\text{Lu}^{\text{II}}$  fragments. This reduction, evidenced by the N–N distance variation, is also highlighted by the nature of the HOMO where two  $d_{xy}$  orbitals overlap with one of the  $\text{N}_2 \pi^*$  while the second  $\pi^*$  orbital overlaps with the  $d_{xz}$  in the LUMO (Figure 7d).

It should be noted that, although **2** presents a very strong affinity for dinitrogen, the  $\text{N}_2$  coordination is reversible with temperature (Figure 7a). Upon heating a solution of **5** in  $\text{tol-}d_8$  to reflux in a sealed NMR tube under an argon atmosphere, the purple color slowly fades away, leading to the orange-red color characteristic of **2**. Agitation of the NMR tube immediately returns the original purple colors, indicating re-coordination of the  $\text{N}_2$  ligand. A movie about this transformation can be found in the Supporting Information section. Reversible  $\text{N}_2$  coordination is unusual in RE dinitrogen complexes, dominated by side-on  $\text{N}_2$  coordination. It has historically been observed in some  $\text{Sm}^{\text{II}}$  complexes,<sup>56</sup> which are less reducing than non-classical  $\text{Ln}^{\text{II}}$  complexes and thus afford weaker  $\text{N}_2$  activation. In the case of RE end-on coordinated  $(\text{N}_2)^{2-}$  complexes, the liberation of  $\text{N}_2$  with concomitant generation, even transiently, of  $\text{Ln}^{\text{II}}$  species seems to be more common and has been observed both thermally<sup>53b,53d</sup> or under UV light irradiation.<sup>53a</sup>

#### Reactivity of **2** towards small molecules: towards $\text{N}_2$ hydrogenation

With the two components of  $\text{H}_2$  splitting and  $\text{N}_2$  reduction to a  $(\text{N}_2)^{2-}$  in hand, we focused on their synergy in relation to  $\text{N}_2$  hydrogenation, relevant to the Haber–Bosch process. We were interested in the reactivity of **5** towards  $\text{H}_2$  as  $\text{Ln}^{\text{III}}$  dinitrogen complexes, which feature formally oxidized metal centers, have been shown to act as “masked” low-valent synthons.<sup>36b,53e,57</sup> In these examples, two-electron reduction processes occurred upon addition of reducible substrates ( $\text{CO}$ ,  $\text{CO}_2$ , aromatic  $N$ -heterocycles), with the systematic release of the  $\text{N}_2$  ligand. Similar reductive reactivity has also been recently reported in the case of  $\text{N}_2$  complexes of  $\text{U}^{\text{IV}}$ ,  $\text{Mg}^{\text{II}}$  and  $\text{Ca}^{\text{II}}$ , where the coordinated and reduced  $(\text{N}_2)^{2-}$  moiety acted as a redox-active ligand, able to reversibly store two electrons.<sup>55,58</sup>

Initial reactivity attempts in NMR tubes showed that heating a purple suspension of **5** in C<sub>6</sub>D<sub>6</sub> under H<sub>2</sub> atmosphere at 80 °C led to the full consumption of **5** over several hours, as evidenced by the formation of a clear colorless solution. <sup>1</sup>H NMR analysis revealed the formation of **3-H** as a major product (*ca.* 90%) along with a minor species (*ca.* 10%) assigned to [Lu(Cp<sup>ttt</sup>)<sub>2</sub>NH<sub>2</sub>] (**6**) (Figure 7a). The identity of **6** was testified by <sup>15</sup>N labelling experiments as well as independent *in situ* synthesis of **6** upon exposure of **2** with NH<sub>3</sub> gas (Figures S18–21). In the <sup>1</sup>H NMR spectrum, the singlet at δ 3.07 ppm for the NH<sub>2</sub> protons in **6** was replaced by a doublet (<sup>1</sup>J<sub>HN</sub> = 62.8 Hz) when performing the experiment with the isotopically labelled **5**-<sup>15</sup>N. Accordingly, the <sup>15</sup>N NMR spectrum of **6**-<sup>15</sup>N showed a triplet at δ 110.1 ppm with the same coupling constant (Figure 7c). In addition, protonolysis experiments with anhydrous HCl confirmed the formation of NH<sub>4</sub>Cl and <sup>15</sup>NH<sub>4</sub>Cl, as evidenced by the presence in the <sup>1</sup>H NMR spectra of the characteristic triplet and doublet signals, respectively, in the range δ 7.2–7.7 ppm (see Figure S24). The origin of the NH<sub>2</sub> hydrogen atoms in **6** and **6**-<sup>15</sup>N was confirmed by reaction of **5** and **5**-<sup>15</sup>N with D<sub>2</sub>, leading to the disappearance of the NH<sub>2</sub> resonance at δ 3.07 ppm while the signals for the Cp<sup>ttt</sup> ligand remained unchanged (Figures S22–23).

As decoordination of the N<sub>2</sub> ligand in **5** is favored with temperature, we hypothesized that the formation of **3-H** might arise from the reaction of *in situ* liberated **2** with H<sub>2</sub>. We reasoned that lower temperatures should be beneficial for higher conversions into **6** vs. **3-H**. Although the reaction appeared kinetically blocked below 0 °C, full conversion was observed upon stirring a toluene or pentane suspension of **5** under H<sub>2</sub> atmosphere over 1–5 days at 0 °C or room temperature. Under these conditions, **6** was consistently formed in 20–32% NMR yields (Figures S22–23).

The exact mechanism of the N<sub>2</sub> hydrogenation reactivity remains elusive to date but control experiments revealed no reaction between **3-H** and N<sub>2</sub> at different temperatures (Figure S25), nor between **3-H** and **5**. Elucidation of the detailed mechanism by DFT studies is in progress and will be reported in due course. Although M–NH<sub>2</sub> moieties have been obtained upon hydrogenation of terminal uranium or iridium nitride complexes,<sup>59</sup> the inaccessibility of oxidation states higher than +III for Lu would prevent the formation of a similar intermediate. As such, the formation of **6** is bound to proceed through direct hydrogenation of the N<sub>2</sub>-ligated complex **5**, an unprecedented reactivity in RE chemistry. The observed N<sub>2</sub>-hydrogenation reactivity is all the more remarkable as it occurs on a doubly-reduced (N<sub>2</sub>)<sup>2-</sup> ligand. So far, the very rare examples of N<sub>2</sub>-functionalization on RE complexes (Figure 1a) have systematically required further activation of the N<sub>2</sub> ligand *via* formation of the (N<sub>2</sub>)<sup>3-</sup> radical anion.<sup>11</sup>

## Conclusion

The present work describes the synthesis and reactivity of a rare example of Lu<sup>II</sup> neutral complex. The fluxionality of the Cp<sup>ttt</sup> ligand is essential to provide kinetic stabilization of the divalent metal center while still allowing coordination of exogenous ligands. The Lu<sup>II</sup> complex, **2**, reduces H<sub>2</sub> at room temperature to give a Lu<sup>III</sup>-hydride complex, which corresponds to the first example of direct H<sub>2</sub>

splitting by a molecular rare-earth complex. This unusual reactivity has been fully supported by DFT calculations. In addition, **2** readily reacts with N<sub>2</sub> with reversible formation of an end-on coordinated (N<sub>2</sub>)<sup>2-</sup> complex. The latter reacts with H<sub>2</sub> under very smooth conditions yielding a Lu<sup>III</sup>-NH<sub>2</sub> *via* direct hydrogenation of the reduced dinitrogen complex. This novel reactivity in RE chemistry, allowing both N≡N bond cleavage and N-H bond formation, opens new avenues for N<sub>2</sub> hydrogenation and functionalization using metals that have so far been neglected for such transformations.

## Associated Content

- Supporting Information: Full experimental details and characterization data, NMR spectra, IR and Raman spectra, UV-vis absorption spectra, EPR spectra, X-ray crystallographic details and DFT calculation details (PDF file).
- Supplementary Data1: Crystallographic data for compounds **1**, **2**, **3-H**, **3-D** and **5** (CCDC reference 2407686-2407690) (CIF file)
- Supplementary Data2: Cartesian coordinates of all DFT computed structures (XYZ file).
- Supplementary Data3: Movie for the reversible transformation of **5** into **2** upon heating (MP4 file).

## Data availability

X-ray crystallographic data for **1**, **2**, **3-H**, **3-D** and **5** are available from the Cambridge Crystallographic Data Centre (CCDC 2407686-2407690) free of charge via <https://www.ccdc.cam.ac.uk/structures/>.

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The manuscript was written through contributions of all authors, and all authors have given approval to the final version of the manuscript.

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