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NH₃ formation from N₂ and H₂ mediated by molecular tri-iron complexes

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Living systems carry out the reduction of N₂ to ammonia (NH₃) through a series of protonation and electron transfer steps under ambient conditions using the enzyme nitrogenase. In the chemical industry, the Haber-Bosch process hydrogenates N₂ but requires high temperatures and pressures. Both processes rely on iron-based catalysts, but molecular iron complexes that promote the formation of NH₃ on addition of H₂ to N₂ have remained difficult to devise. Here, we isolate the tri(iron)bis(nitrido) complex [(Cp'Fe)₃(μ_3 -N)₂] (in which Cp' = η^5 -1,2,4-(Me₃C)₃C₅H₂), which is prepared by reduction of [Cp'Fe(μ -I)]₂ under an N₂ atmosphere and comprises three iron centres bridged by two μ_3 -nitrido ligands. In solution, this complex reacts with H₂ at ambient temperature (22 °C) and low pressure (1 or 4 bar) to form NH₃. In the solid state, it is converted into the tri(iron)bis(imido) species, [(Cp'Fe)₃(μ_3 -NH)₂], by addition of H₂ (10 bar) through an unusual solid-gas, single-crystal-to-single-crystal transformation. In solution, [(Cp'Fe)₃(μ_3 -NH)₂] further reacts with H₂ or H⁺ to form NH₃.

he activation and functionalization of dinitrogen (N₂) as the ultimate source of environmental nitrogen is a challenging but indispensable process for life on our planet. Two leading strategies have been devised for this purpose. The industrial Haber-Bosch process uses a heterogeneous iron-based catalyst operating at high temperatures and elevated pressures for the conversion of H₂ and N₂ to NH₃ (ref.¹⁻³), whereas the iron-containing metalloenzyme nitrogenase accomplishes this transformation by alternating protonation and reduction steps at ambient pressure and temperature⁴⁻⁷. Both systems have been studied extensively with exploration of various molecular model systems^{8,9} based on a variety of elements ranging from boron¹⁰, iron¹¹, cobalt¹² and molybdenum^{13,14} to uranium¹⁵⁻¹⁷. For the early transition metals¹⁸⁻²¹, examples have been established, but an iron nitrido complex that produces NH₃ upon addition of H₂, similar to the industrial Haber-Bosch process, is still lacking. For example, the first iron nitrido species derived from N2 splitting has been described only recently^{22,23}, but formation of NH₃ required subsequent addition of protons and reducing reagents²⁴. Another example of a tri(iron) complex capable of N₂ activation under reducing conditions is [Fe₃Br₃L], in which L is a cyclophane bridged by three β -diketiminate arms; however, the NH₃ release also required protonation to occur²⁵. Similarly, terminally coordinated N₂ ligands may be transformed catalytically to NH₃ in the presence of reductants and a proton source²⁶.

Here, we describe the preparation of $[(Cp'Fe)_3(\mu_3-N)_2]$ (1) (in which $Cp' = \eta^5-1,2,4\text{-}(Me_3C)_3C_5H_2)$ by N_2 cleavage, and its reactivity towards H_2 in solution and in the solid state. In the latter it forms exclusively the H_2 addition product $[(Cp'Fe)_3(\mu_3-NH)_2]$ (2) in a single-crystal-to-single-crystal (SCSC) transformation. Moreover, NH_3 can be generated from 1 and 2 on addition of either H_2 or H^+ in solution.

Results

Synthesis and structural characterization of complex 1. Treatment of $[Cp'Fe(\mu-I)]_2$ (A) with KC₈ in THF under N₂ yields

after recrystallization the tri(iron)bis(nitrido) compound $[(Cp'Fe)_3(\mu_3-N)_2]$ (1) (Fig. 1), which was completely characterized by various spectroscopic measurements and X-ray crystallography. The synergistic interplay of the three iron sites appears to be necessary for the complete cleavage of N₂. This is consistent with previous observations^{22,23,25}, and is further substantiated by the reaction of a related complex $[Cp'FeI(IiPr_2Me_2)]$ (in which $IiPr_2Me_2 = 1,3$ -diisopropyl-4,5-dimethylimidazol-2-ylidene)²⁷. Upon reduction, this complex activates N₂ but leads only to the monomeric N₂ adduct $[Cp'Fe(IiPr_2Me_2)(\eta^1-N_2)]$. The molecular structure of **1** is shown in Fig. 2 and relevant bond distances are provided in the Supplementary Information (Supplementary Fig. 13 and Supplementary Table 2).

The long N...N bond distance of 2.267(2) Å in complex 1 confirms a complete reduction of N₂ to two nitrido ligands that occupy the axial positions of a trigonal bipyramid; the three Cp'Fe fragments lie in the equatorial plane. The atoms N1 and N2 lie 1.15 Å and 1.12 Å, respectively, out of the plane defined by the Fe1, Fe2 and Fe3 atoms, whereas the uniform Fe-Fe bond distances ranging from 2.4727(4) Å to 2.4734(4) Å are consistent with three equivalent Fe sites. Another iron complex containing a μ_3 -bridged nitrido ligand is $[(^{tbs}L)Fe_3(\mu_3-N)]$ (in which $(^{tbs}L)^{6-} = [1,3,5-C_6H_9]$ $(NPh-o-NSi^{t}BuMe_{2})_{3}]^{6-}$, which was isolated from the reaction of $[(^{tbs}L)Fe_3(\mu_3-N)(\mu_2-Br)_2]$ with KHB(sec-Bu)₃ under an N₂ atmosphere²⁸. By contrast, when the precursor $[(^{tbs}L)Fe_3(\mu_2-Br)(\mu_3-Br)$ (Br)] was reduced with KC₈ under N₂, the iron imido complex $[(^{tbs}L)Fe_3(\mu_2-NH)_3]$ was isolated (presumably as a result of protonation)²⁵. Overall, the structural motif with μ_3 -bound N atoms is a molecular model related to the Fe(110) surface encountered in the Haber-Bosch process²⁹⁻³¹.

Electronic ground-state properties of complex 1. Zero-field ⁵⁷Fe Mössbauer measurements on **1** (Fig. 3a and Supplementary Fig. 24) show a single doublet of Lorentzian lines and therefore confirm

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Fig. 1 Synthesis and reactivity of compound 1 towards H_2 in solution and in the solid state, producing compounds 2, 3 and NH_3 . N_2 splitting occurs under reducing conditions to form the tri(iron)bis(nitrido) complex 1. In solid state, 1 reacts with H_2 to form the tri(iron)bis(imido) species 2, whereas in solution with H_2 it forms the tri(iron)bis(imido) species 2, the bis(iron)bis(nitride) 3 and NH_3 .



Fig. 2 | Molecular structures of compound 1 and compound 2. For both complexes, the structures show the splitting of the N₂ molecule and its relative arrangement within a core of three iron atoms (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms are removed for clarity except those connected to N1 and N2 in complex 2.

that all iron sites in 1 are virtually equivalent, a finding that is also derived from our X-ray crystallographic data (see above). The values obtained at T = 20 K for the isomer shift ($\delta_{iso} = 0.454(1)$ mm s⁻¹) and the quadrupole splitting ($\Delta E_0 = 0.669(1) \text{ mm s}^{-1}$) are consistent with those found for other iron complexes in the +III oxidation state (Supplementary Table 5 and references therein). However, an unambiguous assignment of the spin state based solely on these Mössbauer parameters is difficult. Hence, solid-state magnetic susceptibility measurements on compound 1 were conducted between temperatures of T=3 and 300 K. The effective magnetic moment (μ_{eff}) above approximately T = 100 K shows only small variations with temperature (Supplementary Fig. 17), and the observed value of $\mu_{\rm eff} = 3.22 \,\mu_{\rm B}$ at $T = 300 \,\rm K$ is close to the spin-only value of $\mu_{\rm eff} = 3.00$ $\mu_{\rm B}$ for three (paramagnetic) S=1/2 spin centres per molecule, which supports the presence of three low-spin (S=1/2) iron(III) centres in complex 1. Furthermore, a decreasing μ_{eff} value when the temperature is below approximately T = 50 K implies weak (intramolecular) antiferromagnetic coupling (with coupling strength

of $J=-1.36 \text{ cm}^{-1}$) between the individual iron centres to form a ground state at T=3 K with $\mu_{\text{eff}}=2.33 \mu_{\text{B}}$, corresponding to a total spin per molecule of $S_t=1/2$ (see Section 6 in the Supplementary Information for details). This conclusion is corroborated further by an X-band electron paramagnetic resonance (EPR) spectrum that was recorded at T=5 K in frozen solution (Supplementary Fig. 15).

Reactivity of complex 1 towards H₂ in solution and in the solid state. Exposure of 1 to HCl produces 70–76% NH₄Cl, which was quantified by the indophenol protocol (Supplementary Table 1 and Supplementary Fig. 1)³². This is similar to the previously reported nacnac-stabilized iron complex [{(nacnac)Fe}₃(μ_3 -N)(μ_2 -N) (KCl)₂(Fe(nacnac))] (in which nacnac = MeC[C(Me)N(2,6-Me ₂C₆H₃)]₂)^{22-24,33,34}. Moreover, whereas complex 1 is stable under an N₂ and Ar atmosphere, it reacts in hexane solution with H₂ (about 4 bar) to form NH₃ with a yield of about 3–7%, and the NH₃ yield can further be increased to about 10% when this hydrogenation reaction is carried out in THF (Supplementary Table 1). Nevertheless,

the relatively low NH₃ yield is attributed to the instability of 1 in the presence of NH₃, which induces decomposition to form Cp'H and $[Cp'Fe(\mu-N)]_{2}^{35}$; this was independently verified by addition of NH₃ to 1. Isotopic labelling was performed using ¹⁵N-labelled 1 and D₂ (where D represents deuterium or ²H), and we detected ¹⁵ND₃ and DCp' in the ²H NMR spectrum (Supplementary Fig. 4). Two organometallic species, the mixed-valent tri(iron)bis(imido) species $[(Cp'Fe)_3(\mu_3-{}^{15}ND)_2]$ (2- ${}^{15}N$,D), and the dimeric iron(IV) nitrido complex $[Cp'Fe(\mu^{-15}N)]_2$ (3-¹⁵N)³⁵ are formed in the ratio 1:2 (as determined by ¹H NMR spectroscopy). Owing to their very similar solubilities, only minor quantities of both species could be isolated, preventing a closer examination of their intrinsic physicochemical properties. However, 3 can be prepared independently from the reaction of $[Cp'Fe(\mu-I)]_2$ with NaN₃ and exhibits no reactivity towards H₂ even at elevated pressures³⁵. Therefore, **3** is not involved in formation of NH₃, which leaves the tris(iron)bis(imido) complex 2 as a possible intermediate in this process.

Synthesis and structural characterization of complex 2. Every attempt to obtain complex 2 from complex 1 using standard H-atom donors in solution failed, but exposure of 1 to H_2 in the solid state resulted in a clean conversion to 2. Furthermore, no NH₃ could be detected in the gas phase. The iron imido species 2 (whose molecular structure is shown in Fig. 2 and Supplementary Fig. 14) can be recrystallized from diethyl ether. The metrical parameters of complex 2 differ from those of complex 1 only slightly, but a few notable features should be mentioned. The Fe-Fe distances can be grouped into two slightly shorter bonds of 2.5195(4) Å and 2.5284(4) Å for Fe1-Fe2 and Fe2-Fe3, respectively, and a slightly longer bond of 2.5408(4) Å for Fe1-Fe3, implying that two different iron sites are present in a 2:1 ratio. The N1...N2 distance is also significantly increased from 2.267(2) Å to 2.352(3) Å on addition of H₂. The overall structural feature of a trigonal bipyramid with three Cp'Fe moieties occupying the equatorial plane is conserved. We also carried out this transformation as an SCSC process, which was experimentally supported by the minor changes in the cell dimensions of 1 and 2 (Supplementary Table 2). This is a rare example of an SCSC reaction in organometallic compounds³⁶⁻⁴⁰; this system thereby resembles the heterogeneous Haber-Bosch process, in which surface-bound iron imido species are formed on addition of H₂. However, when the reduction of $[Cp'Fe(\mu-I)]_2$ with KC₈ in THF is carried out under a mixture of H2 and N2, only the di(iron) tetrahydride $[Cp'Fe(\mu-H)_2]_2$ is isolated^{41,42}, preventing direct formation of NH₃ from H₂ and N₂.

Experimental determination of the barrier to H₂ addition to complex 1 in the solid state. The process of H₂ addition can be monitored further by zero-field 57Fe Mössbauer (Fig. 3) and solid-state ¹⁵N Hahn-echo magic angle spinning (MAS) NMR spectroscopy (Fig. 4). As a starting point, when the reduction of $[Cp'Fe(\mu-I)]_2$ is carried out in a ¹⁵N, atmosphere, the ¹⁵N-labelled tri(iron) bis(nitrido) species (1-¹⁵N) is isolated. Two resonances at $\delta = 1,520$ and 1,400 ppm can be found in the solid-state ¹⁵N NMR spectrum, reflecting the different chemical environments of the two N atoms (Fig. 4c and Supplementary Figs. 8, 10, 11). Note that fast paramagnetic relaxation prevents ¹⁵N NMR spectra from being recorded in solution. Exposure of $1\ensuremath{1^{-15}N}$ to H_2 results in a slow decrease of ¹⁵N NMR resonance lines attributed to 1-¹⁵N, whereas a new resonance line appears at $\delta = -256$ ppm that is attributed to the tri(iron) bis(imido) species (2-15N) (Fig. 4b and 4a and Supplementary Figs. 10-12). As with 1-15N, no 15N NMR resonance was detected for 2-15N when these measurements were carried out in solution. To obtain further insights into the kinetics of this transformation from 1 to 2, zero-field Mössbauer measurements were executed on a series of samples with different H₂ exposure times between 15 min and 14 d. The line shape of the Mössbauer spectra changes



Fig. 3 | Conversion of complex 1 into complex 2 upon different H₂ exposure times followed by Mössbauer spectroscopy. a, Selected zero-field Mössbauer spectra for the conversion of 1 (green line for three equivalent Fe(III) sites) into 2 (orange line for two Fe(II) sites and red line for one Fe(III) site) after different H₂ (10 bar) reaction times recorded at T = 20 K. A small, but so far unidentified, impurity with a volume fraction ranging between 2 and 4% was visible in all H₂-treated compounds (10 bar). However, for clarity, the sub-spectrum of this impurity is not shown in the figure (see Supplementary Fig. 25 for further details, including the sub-spectrum of the impurity). Grey circles, experimental data; lines, fit with doublets of Lorentzian lines adapting a model described in the text. b, Consumption and formation of 1 and 2 plotted against H₂ exposure time. Respective volume fractions of 1 (green circles) and 2 (orange circles) were determined by Mössbauer spectroscopy at T = 20 K (Supplementary Table 4). Black and grey stars indicate volume fractions for a sample that was obtained after an H₂ exposure time of 24 h and with an applied H₂ pressure of 80 bar. Lines are fits with an exponential decay (green) or an exponential growth law (red) with rate constants of 0.079(14) and 0.078(10) h⁻¹, respectively.

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Fig. 4 | Complete conversion of ¹⁵**N**-**labelled 1 into 2 as monitored by** ¹⁵**N Hahn-echo MAS NMR spectra. a**, After 10 d with 10 bar of H₂ (full conversion to [(Cp'Fe)₃(μ_3 -¹⁵**N**H)₂] (**2**-¹⁵**N**)). **b**, After 24 h (mixture of [(Cp'Fe)₃(μ_3 -¹⁵**N**)₂] (**1**-¹⁵**N**) and [(Cp'Fe)₃(μ_3 -¹⁵**N**H)₂]) (**2**-¹⁵**N**)). **c**, Before addition of H₂ to [(Cp'Fe)₃(μ_3 -¹⁵**N**)₂] (**1**-¹⁵**N**). Spinning rate is 16 kHz; relaxation delay is 1s; SSB, spinning side band.

systematically over the exposure time, as shown by representative spectra in Fig. 3a. However, the quantitative analysis is complicated because of the very similar Mössbauer parameters obtained for complexes 1 and 2 (Supplementary Table 4). Therefore, we postulated that (1) the sub-spectrum representing residual amounts of 1 in the reaction mixture can be described by the same Mössbauer parameters as for pure compound 1, (2) the binding of two H atoms in 2 results in two Fe(II) centres whereas one iron site remains in the +III oxidation state, (3) both Fe(II) sites are equivalent, (4) the relative signal intensities of the Fe(II) and Fe(III) centres in complex 2 adopt a 2:1 ratio, and (5) the sub-spectra of complex 2 in the reaction mixture can be described by the same Mössbauer parameters as for pure compound 2. The result of this analysis is shown in Fig. 3 and Supplementary Table 4. The experimental and theoretical data are consistent with the model advanced above. Based on the relative amounts of complexes 1 and 2 as a function of different H₂ exposure times (Fig. 3b), and assuming pseudo-first-order kinetics and the Eyring equation⁴³, the barrier to H₂ addition is estimated to be ΔG^{\ddagger} $(295 \text{ K}) = 23.7(2) \text{ kcal mol}^{-1} (\Delta \text{G} \text{ is the change in Gibbs free energy})$ and ‡ denotes a transition state).

Electronic ground-state properties of complex 2. The two subspectra in the Mössbauer spectrum that is associated with complex 2 (Fig. 3a) are attributed to the presence of two iron sites with different oxidation and spin states. The first iron site is described by an isomer shift of $\delta_{iso} = 0.369(5) \text{ mm s}^{-1}$ and quadrupole splitting of $\Delta E_Q = 0.563(8) \text{ mm s}^{-1}$, which are close to the values found for complex 1, implying an Fe(III) site and an S = 1/2 spin state. For the second iron site, a more positive isomer shift of $\delta_{iso} = 0.565(3) \text{ mm s}^{-1}$ was determined, which is consistent with those found for rare Fe(II) intermediate-spin (S = 1) complexes⁴⁴. The presence of two Fe(II) atoms in compound 2, which adopt an intermediate spin of S = 1, is also corroborated by density functional theory (DFT) and complete active space self-consistent field (CASSCF) computations, indicating a complex coupling scenario between two Fe(II), S = 1 and one Fe(III), S = 1/2 spin centres (that is, S = 1 - (1 - 1/2) = 1/2), in which one electron is delocalized between two iron atoms (see Section 8 in the Supplementary Information for details). Consistent with this, the quadrupole splitting value of $\Delta E_0 = 0.384(11) \text{ mm s}^{-1}$ associated with the two Fe(II) sites in compound 2 is very small, which also suggests substantial covalent contributions to the electric field gradient at the 57Fe nucleus site45. To provide further experimental support for these spin- and oxidation-state assignments, solid-state magnetic susceptibility measurements were conducted on compound 2 (obtained after 10d of H₂ (10bar) exposure) at temperatures between T = 3 and 300 K. Considering three uncoupled spins at ambient temperature, the observed value of $\mu_{eff} = 5.47 \,\mu_{B}$ at $T = 300 \,\text{K}$ is in line with the spin-only value of $\mu_{\text{eff}} = 4.36 \,\mu_{\text{B}}$ for two S = 1 and one S = 1/2 spin centres. The larger experimentally observed value is ascribed to low-lying unquenched orbital contributions attributed to the two paramagnetic Fe(II) sites. Furthermore, a marked decrease in μ_{eff} values is observed with decreasing temperature (Supplementary Fig. 20), and suggests substantial (intramolecular) antiferromagnetic coupling between the individual spin centres of 2 and/or the presence of zero-field splitting (ZFS) caused by the Fe(II) intermediate-spin (S=1) sites. An analysis revealed an estimation for the ZFS parameters $(D=136 \text{ cm}^{-1}, E/D=0)$ and the coupling strength $(J = -3.5 \text{ and } -0.7 \text{ cm}^{-1})$ acting between the individual spin centres (see Section 6 in the Supplementary Information for details). Similarly to complex 1 (see above), the effective magnetic moment of $\mu_{\text{eff}} = 2.36 \mu_{\text{B}}$ at T = 3 K and the recorded X-band EPR spectrum of complex 2 in frozen solution at T = 5 K (Supplementary Fig. 16) are consistent with the formation of a ground state with a total spin per molecule of $S_t = 1/2$.

Reactivity of complex 2 towards H_2 in solid state and solution. No H/D exchange occurs when D_2 is added to **2** in the solid state. As with complex **1** (see above), the addition of HCl to **2** forms NH₄Cl in a similar 75–80% yield (Supplementary Table 1). When hexane solutions of **2** were exposed to H_2 (about 4bar) and the

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Fig. 5 | Computed enthalpy profile at room temperature for the reaction of complex 1 with H₂ **to yield compound 2.** The Gibbs free energy (Δ G) values for the intermediates (**A**-**E**), transition states (labelled with [‡] in the text) and final product **F** (complex **2**) are given in brackets. Iron, pale red; nitrogen, pale blue; carbon, light grey; hydrogen atoms in the H₂ molecule undergoing heterolytic cleavage, red and orange. Heterolytic H₂ cleavage promoted by complex **1** yields the tris(iron)(hydrido)(intrido) intermediate **B**, which readily rearranges to intermediate **C** featuring a (μ ₂-NH, μ ₂-H) coordination mode. Hydride transfer to the Cp' ring via the transition state **TSCD** results in species **D**, which converts to the slightly favoured isomer **E**. In the last step the Cp' ligand delivers a proton to the second nitrido functionality via transition state **TSE2** to yield the final product **2**.

volatile material was vacuum-transferred at ambient temperature, a minor quantity of NH_3 (about 0.5%) was detected, which increased to about 5%, when the residue was heated. This feature implies that iron-containing species are formed that incorporate coordinated NH_3 , which requires elevated temperatures to be released (Supplementary Table 1). Nevertheless, our results establish that both compounds 1 and 2 can form NH_3 on addition of H_2 , but complex 1 is much more reactive than 2 and the pathways may be different.

Computational studies. To gain additional insights into the solid-state reactivity of 1 with H₂ and therefore to propose a plausible mechanism for the formation of 2, DFT (B3PW91; Fe, SDDALL; other atoms, 6-31G(d,p)) computations were performed (Fig. 5). This functional has proven its ability to properly describe geometry, electronic structure and reaction mechanisms involving iron complexes^{35,46}. Several processes were computed and found to be not kinetically viable (see Supplementary Fig. 26 for details). We also probed whether the two H atoms originate from one molecule of H₂ and whether the Cp' ligand is actively involved in the H-atom transfer process by acting as a proton transfer relay. The first step of the reaction involves heterolytic H₂ cleavage by one nitrido functionality in 1. This process is associated with a low activation barrier $(\Delta_r H^{\ddagger} = 4.8 \text{ kcal mol}^{-1}; \Delta_r G^{\ddagger} = 8.5 \text{ kcal mol}^{-1})$, which is consistent with a distinct nucleophilicity of the nitrido moiety. Furthermore, this reactivity is reminiscent of that observed for {([PhBP3] $Fe_{2}(\mu_{2}-N)$ {Na(THF)₅} (in which [PhBP3] = PhB(CH_{2}PPh_{2})_{3}) yielding {([PhBP3]Fe)₂(μ_2 -NH)(μ_2 -H)}{Na(THF)₅}⁴⁷. To accommodate this reaction, the nitrido N atom in 1 undergoes a μ_3 - to μ_2 -(edge) migration at the first transition state (TS). In contrast, a

direct activation of H_2 by the μ_3 -bridging N atom increases the barrier to $\Delta_r H^{\dagger} = 42.6 \text{ kcal mol}^{-1}$ ($\Delta_r G^{\dagger} = 48 \text{ kcal mol}^{-1}$, Supplementary Fig. 26), which contradicts the experimentally observed reaction barrier of $\Delta G^{\ddagger}(295 \text{ K}) = 23.7(2) \text{ kcal mol}^{-1}$ (see above). Furthermore, it also illustrates the mobility of the bridging N atoms above the plane formed by the three Cp'Fe fragments. The trinuclear arrangement of 1 facilitates this rearrangement and allows it to occur in the solid state. Following the reaction coordinate leads to a tris(iron) (hydrido)(imido)(nitrido) intermediate, **B**, that readily forms **C** with a $(\mu_2$ -NH, μ_2 -H) coordination mode. To account for the formation of 2, a 'carambole' mechanism⁴⁸, involving the transient migration of a hydrogen to the Cp' ring, was investigated computationally starting from intermediate C. The feasibility of proton transfer to a Cp ring was also established previously for $[(\eta^5-C_5Me_5)_2Co]$ in the context of catalytic N₂-to-NH₃ formation, in which the metallocene facilitates a process of proton-coupled electron transfer (PCET)^{49,50}. More recent studies also established the feasibility of an H-atom transfer reaction in iron indenyl half-sandwich complexes⁵¹. Hence, we computed a mechanism that involves a hydride-to-proton 'umpolung' reaction. The hydride transfer to the Cp' ligand and therefore the conversion of C to D proceeds via transition state **TSCD** and has a low activation barrier of $\Delta_r H^{\ddagger} = 12.9 \text{ kcal mol}^{-1}$, which is in agreement with the results of a previous study⁴⁸. After minor rearrangements, intermediate D converts to the slightly more stable isomer E. In the last step, intermediate E transforms into the final product 2, and the Cp' ligand delivers the proton directly to the second nitrido via transition state TSE2. Therefore, the presence of the Cp' ligand is crucial for the H-atom transfer process, and otherwise the reaction stops at intermediate C. The barrier for the last step is the highest in the reaction profile ($\Delta_r H^{\ddagger} = 29.6 \text{ kcal mol}^{-1}$;

 $\Delta_r G^{\ddagger}$ = 34.9 kcal mol⁻¹), and agrees with the experimentally determined barrier of $\Delta G^{\ddagger}(295 \text{ K}) = 23.7(2)$ kcal mol⁻¹ (see above). Note that in this last step the nitrido again alternates between a μ_3 - and a μ_2 -bridging mode. The overall reaction is very exothermic ($\Delta_r H = -45.7$ kcal mol⁻¹), which is consistent with the lack of H/D exchange when the complex is exposed to D_2 (see above).

Summary

We present a molecular tri(iron)bis(nitrido) complex that reacts with H_2 to form NH₃. The initial step of H_2 addition, which converts the tri(iron)bis(nitrido) complex into the mixed-valent tri(iron) bis(imido) species, occurs in a rare SCSC transformation. This process was followed by NMR and Mössbauer spectroscopy, allowing the barrier of the addition of H_2 to be evaluated experimentally. For the solid-state conversion of complex 1 to complex 2, additional DFT studies were conducted. Some key features that emerge from these computations are: (1) H_2 splitting occurs along an Fe–N edge; (2) the flexibility of the N atoms is essential for a μ_3 - to μ_2 -(edge) migration above the (Cp'Fe)₃ moiety, significantly lowering the barrier of this process to form an intermediate with a (μ_2 -NH, μ_2 -H) coordination mode; and (3) the Cp' ligand is not a spectator but actively participates as a proton relay in the H-atom transfer to the μ_3 -bound N atom by a 'carambole' mechanism.

Online content

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Methods

General considerations. All synthetic and spectroscopic manipulations were carried out under an atmosphere of purified N₂ or Ar, in either a Schlenk apparatus or a glovebox. Solvents were dried and deoxygenated either by distillation under a nitrogen or argon atmosphere from sodium benzophenone ketyl (for THF, pentane, hexane, diethyl ether) or by an MBraun GmbH solvent purification system (for all other solvents). Deuterated solvents were dried with sodium under an N₂ or an Ar atmosphere, vacuum-transferred, freeze-pump-thaw degassed and stored under N₂ or Ar. Elemental analyses were performed by combustion and gas chromatographic analysis with an elementar varioMICRO or elementar varioMICRO CUBE instrument. [Cp'FeI]₂ and KC₈ were prepared according to procedures reported in the literature^{52,53}.

NMR studies. Quick pressure valve NMR tubes were used for the reactions with H₂ in solution. NMR spectra were collected on Bruker machines (OV500 and AV400). Solid-state NMR experiments were recorded at the Laboratoire de Chimie de Coordination (Toulouse) on a Bruker Avance III HD 400 spectrometer equipped with a 3.2 mm MAS probe at ambient temperature. Samples were spun between 10 kHz and 16 kHz at the magic angle using ZrO2 rotors. ¹H, ²H and ¹³C MAS spectra were recorded with recycle delays of 1 s, 0.5 s and 0.2 s, respectively. ¹⁵N Hahn-echo experiments were synchronized with the spinning rate (16kHz) and with a recycle delay of 1 s. ¹⁵N CP and HETCOR MAS experiments were performed with a recycle delay of 1.5 s and contact times of 3 ms and 1 ms, respectively. The ²H spectrum was fitted using the DMFIT software⁵⁴. To study the addition of H₂ to complex 1 in the solid state, a ZrO₂ rotor was charged with $[(Cp'Fe)_3(\mu_3-N_2)]$ (1) (about 80 mg) and the initial solid-state NMR spectra were recorded. The rotor was then opened and exposed to H₂ (10 bar) for 1 d and then for an additional 9d. The reaction progress of the identical sample was monitored by solid-state NMR spectroscopy.

Crystallographic studies. Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of an Oxford Diffraction Nova A diffractometer. Intensity data were recorded at 100 K using mirror-focussed Cu K_a radiation (λ = 1.54184 Å). Absorption corrections were based on multi-scans. Structures were refined anisotropically on F² using the program SHELXL-2017 (ref.⁵⁵). The NH hydrogen atoms were refined freely but with a common isotropic temperature factor. Other hydrogens were included using rigid idealized methyl groups or a riding model. For further refinement details see Section 4 ('Crystallographic details') in the Supplementary Information.

X-band EPR studies. X-band EPR spectra were recorded on a Bruker EMX spectrometer with an OXFORD ESR900 continuous-flow cryostat. Frozen toluene and methylcyclohexane solutions of complexes 1 and 2, respectively, were prepared in quartz tubes (707-SQ-250M, Wilmad-LabGlass). The experimental spectra were simulated with EasySpin 5.2.2 (ref.⁵⁶).

Solid-state magnetic susceptibility studies. Solid-state magnetic susceptibility studies were performed on a Cryogenic closed-cycle SQUID magnetometer between T = 2.6 K and 300 K with an externally applied magnetic field of $H_{\rm ext} = 1$ kOe. The samples were prepared in quartz tubes as described previously⁵⁷, and the diamagnetic background signal of an empty sample holder including quartz wool was determined experimentally and subtracted from the raw magnetization data. The experimental data were also corrected for the overall diamagnetism of the investigated molecules using tabulated Pascal constants³⁸. To ensure the validity of the Curie law approximation for an applied magnetic field of $H_{\rm ext} = 1$ kOe, supplementary measurements at T = 2.6 K with applied magnetic fields between $H_{\rm ext} = 0.05$ kOe and 10 kOe were also executed (Supplementary Figs. 19,22).

57Fe Mössbauer studies. Zero-field 57Fe Mössbauer measurements were performed on a standard Halder and WissEl transmission spectrometer with sinusoidal velocity sweep. Velocities were calibrated using an α -Fe foil at T = 300 K and confirmed by supplementary room-temperature measurements with powders of sodium nitroprusside (Na2[Fe(CN)2NO] • 2H2O) or potassium ferrocyanide $(K_4[Fe(CN)_6] \bullet 3H_2O)$ at T = 300 K. Polycrystalline powders were prepared with an area density corresponding to about $0.25-0.34\,\mathrm{mg}^{57}\mathrm{Fe}\,\mathrm{cm}^{-2}$ and were stored in sample containers made of Teflon or polyether ether ketone (PEEK). The temperature-dependent measurements were conducted on a CryoVac continuous-flow cryostat (CFC) or a Janis closed-cycle cryostat (CCC) with helium exchange gas (adjusted to approximately 100 mbar during the measurement). The temperature was recorded with a calibrated Si diode located close to the sample container, and indicated variations of less than 0.1 K during the experiment. The minimum experimental line width (full width at half maximum, or FWHM) was < 0.24 mm s⁻¹ (in the case of the CryoVac CFC setup) or < 0.27 mm s⁻¹ (in the case of the Janis CCC setup). The Mössbauer source, with nominal activity of about 50 mCi of 57Co in a rhodium matrix, was stored at ambient temperature during the measurement. Isomer shifts (δ_{iso}) are quoted relative to metallic iron at T = 295 K but were not corrected in terms of the second-order Doppler shift. The spectra

were analysed by least squares fitting with doublets of Lorentzian lines using the software package NORMOS⁵⁹.

Computational studies. All DFT calculations were carried out with the Gaussian 16 suite of programs⁶⁰. Geometries were fully optimized in the gas phase without symmetry constraints using the B3PW91 functional^{61,62}. The nature of the extrema was verified by analytical frequency calculations. The calculations of electronic energies and enthalpies of the extrema of the potential energy surface (minima and transition states) were performed at the same level of theory as the geometry optimizations. Intrinsic reaction coordinate (IRC) calculations were performed to confirm the connections of the optimized transition states. Iron atoms were treated with a Stuttgart effective core potential augmented with a polarization function ($\zeta_f = 2,462$)^{63,64}. For the other elements (H, C and N), Pople's double- ζ basis set 6-31G(d,p) was used^{65,66}. The electronic charges (at the DFT level) were computed using the natural population analysis technique⁶⁷.

Synthesis of [(Cp'Fe)₃(µ₃-N₂)] (1). KC₈ (272 mg, 2.00 mmol, 2 eq.) and THF (10 ml) were added to a bomb flask equipped with a magnetic stirring bar. The bomb vessel was cooled in a liquid nitrogen bath (77 K), and when the suspension was completely frozen, a solution of [Cp'FeI]2 (832 mg, 1.00 mmol, 1 eq.) in THF (10 ml) was added slowly to the bomb flask under a stream of N2. The flask was sealed, removed from the cold bath and allowed to slowly warm to room temperature while the mixture was stirred. During this time the colour of the suspension changed from light brown to red and finally to olive green. After the suspension was stirred at ambient temperature for 30 min, the N₂ pressure was released slowly to the Schlenk line and the solvent was removed under dynamic oil pump vacuum. The green-brown residue was extracted with hexane (4 ×10 ml) and filtered. The solvent was again removed under dynamic oil pump vacuum and the green-brown solid was re-dissolved in a minimum amount of Et₂O (about 10 ml) and stored for crystallization at -30 °C to yield fine dark green needles. The yield was 53% (310 mg, 0.35 mmol). When the reaction was carried out at room temperature under 1 atm of N₂, complex 1 was isolated with about 20% yield (besides significant quantities of [Cp'2Fe]). Complex 1 was stable under an N2 and Ar atmosphere for several months without any sign of decomposition. Mp: 174 °C (dec.). Elemental analysis (%) for C₅₁H₈₇Fe₃N₂: calculated, C 68.38, H 9.79, N 3.13; found, C 67.89, H 9.75, N 3.14. The EI mass spectrum showed a molecular ion at m/z = 895 amu. UV/Vis (n-hexane, 22 °C, nm): 216 (ε = 38,800 l mol⁻¹ m⁻¹), 252 (ε = 34,000 l mol⁻¹ cm⁻¹), 282 (ε = 33,800 l mol⁻¹ cm⁻¹), 315 (ε = 40,800 l mol⁻¹ cm⁻¹), 375 (sh, $\varepsilon = 16,200 \,\mathrm{lmol^{-1} \, cm^{-1}}$), and 667 ($\varepsilon = 1,770 \,\mathrm{lmol^{-1} \, cm^{-1}}$). ¹H NMR (C₆D₁₂, 298 K): $\delta = 7.37$ (s, br, 6 H, ring-CH, $\nu_{1/2} = 360$ Hz), 0.20 (s, br, 54 H, tBu-H, $\nu_{1/2} = 100$ Hz), -1.68 (s, br, 27 H, *t*Bu-*H*, $\nu_{1/2}$ =60 Hz) ppm. ¹⁵N Hahn-echo MAS NMR: δ =1,520, 1,403 ppm. For further details see Section 3 ('Solid-state NMR studies') in the Supplementary Information.

When complex 1 was exposed to small amounts of H₂O, we observed the formation of [{Cp'Fe(μ_2 -OH)}₃]^{ss} besides considerable decomposition. This contrasts with the behaviour of 1 when exposed to Ar, N₂ or H₂, during which the formation of [{Cp'Fe(μ_2 -OH)}₃] was not observed.

Synthesis of [(Cp'Fe)₃(μ_3 -NH)₂] (2). Either a powder or crystals of [(Cp'Fe)₃(μ_3 -N₂)] (100 mg, 0.11 mmol) were pressurized with H₂ (10 bar) for 14 d at ambient temperature. When the reaction was performed on crystalline material, an SCSC transformation occurred. Complex 2 was stable under an N₂ and Ar atmosphere for several months without any sign of decomposition. Mp: 197 °C (dec.). The EI mass spectrum showed a molecular ion at *m*/*z*=897 amu. UV/Vis (*n*-hexane, 22 °C, nm): 222 (ε = 35,2001mol⁻¹ cm⁻¹), 275 (sh, ε = 22,0001mol⁻¹ cm⁻¹), 360 (ε = 19,0001mol⁻¹ cm⁻¹), 399 (ε = 20,9001mol⁻¹ cm⁻¹), and 680 (sh, ε = 1,0501mol⁻¹ cm⁻¹). 'H NMR (C₆D₁₂, 298 K): δ = 1.00 (s, br, $\nu_{1/2}$ =70 Hz), 0.59 (s, br, $\nu_{1/2}$ =50 Hz), 0.48 (s, br, $\nu_{1/2}$ =70 Hz), 0.27 (s, br, $\nu_{1/2}$ =70 Hz), 0.02 (s, br, $\nu_{1/2}$ =50 Hz), and -0.60 (s, br, $\nu_{1/2}$ =30 Hz) ppm. ¹⁵N Hahn-echo MAS NMR: δ = -256.2 ppm. For further details see Section 3 ('Solid-state NMR studies') in the Supplementary Information.

General procedure for the reaction of compounds 1 and 2 with H₂. A solution of 1 (or 2) (40 mg, 0.045 mmol) in hexane (10 ml) was loaded in a bomb flask and cooled in liquid nitrogen (77 K). The bomb flask was then evacuated, refilled with H₂ (1 bar), and closed tightly. After the flask had thawed to ambient temperature, the H₂ pressure had increased to about 4 bar and the reaction was stirred for 24 h at room temperature. All volatiles (solvent, hydrolysed ligand and NH₃) were carefully transferred in vacuum onto a frozen solution of HCl in Et₂O (2.0 M). After the solution was thawed, the solvent was removed by oil pump vacuum. The remaining NH₄Cl was dissolved in H₂O (1,000 µl). Afterwards, 20 µl (or 40 µl) aliquots were used for each titration of the indophenolic titration of NH₃³². All reactions were carried out three times with the same batch of compounds 1 and 2, and therefore three different entries are listed in Supplementary Table 1. To ensure reproducibility, three independent runs were performed with the same batch.

General procedure for the reaction of compounds 1 and 2 with HCl. In the first method, a solution of **1** (or **2**) (40 mg, 0.045 mmol) in hexane (or THF) (10 ml) was

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loaded in a bomb flask, cooled in liquid nitrogen, treated with 1 ml of a solution of HCl in Et₂O (2.0 M) and closed tightly. After thawing to ambient temperature, the mixture was stirred for 1 h. All volatiles (solvent, hydrolysed ligand and NH₃) were carefully transferred in vacuum onto a frozen solution of HCl in Et₂O (2.0 M), and the residue was heated extensively (>450 °C) to decompose the formed NH₄Cl. After the mixture was thawed to ambient temperature, the solvent was removed by oil pump vacuum. The remaining NH₄Cl was dissolved in H₂O (1,000 µl). Afterwards, 40 µl aliquots were used for each titration of the indophenolic titration of NH₃ (ref.³²). All reactions were carried out three times with the same batch of compounds 1 and 2, and therefore three different entries are listed in Supplementary Table 1. To ensure reproducibility, three independent runs were performed with the same batch.

In the second method, a solution of 1 (or 2) (40 mg, 0.045 mmol) in hexane (10 ml) was loaded in a bomb flask, cooled in liquid nitrogen, treated with 1 ml of a solution of HCl in Et₂O (2.0 M) and closed tightly. After thawing to ambient temperature, the mixture was stirred for 1 h. Afterwards, 40 µl aliquots were used for each titration of the indophenolic titration of NH₃ directly from the reaction mixture¹². The two methods delivered the same yields of ammonia during the reaction with HCl. All reactions were carried out three times with the same batch of compounds 1 and 2, and therefore three different entries are listed in Supplementary Table 1. To ensure reproducibility, three independent runs were performed with the same batch. Yields for $[(Cp'Fe)_3(\mu_3-N_2)]$ (1) after addition of H₂ were 3–10% and after addition of HCl were 70–76% (see Supplementary Table 1 for details). Yields for $[(Cp'Fe)_3(\mu_3-NH)_2]$ (2) after addition of H₂ (about 5%) and after addition of HCl were 75–80% (see Supplementary Table 1 for details).

Data availability

The authors declare that all of the data supporting the findings of this study are available within the paper and the Supplementary Information, and also from the corresponding authors upon reasonable request. This includes experimental details, NMR studies in solution, solid-state NMR studies, crystallographic details, X-band EPR studies, solid-state magnetic susceptibility studies, zero-field ⁵⁷Fe Mössbauer studies, and computational details. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers 1939746 (1) and 1939747 (2). Copies of the data can be obtained free of charge at https://www.ccdc. cam.ac.uk/structures.

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Author contributions

M.R., D.B., Y.C., S.B. and M.D.W. conceived the experiments; M.R., D.B., K.M., M.-K.Z., M.F., P.G.J., Y.C., S.B. and M.D.W. designed and performed experiments and analysed the data; I.d.R. and L.M. performed computational studies; M.R., D.B., S.B., L.M. and M.D.W. wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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