Selectivity of tungsten mediated dinitrogen splitting vs. proton reduction†

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Mo complexes are currently the most active catalysts for nitrogen fixation under ambient conditions. In comparison, tungsten platforms are scarcely examined. For active catalysts, the control of N2 vs. proton reduction selectivities remains a difficult task. We here present N2 splitting using a tungsten pincer platform, which has been proposed as the key reaction for catalytic nitrogen fixation. Starting from [WCl3(PNP)] (PNP = N(CH2CH2PtBu2)), the activation of N2 enabled the isolation of the dinitrogen bridged redox series (N2)WCl(PNP)). Protonation of the neutral complex results either in the formation of a nitride [W(N)Cl(HPNP)] or H2 evolution and oxidation of the W2N2 core, respectively, depending on the acid and reaction conditions. Examination of the nitrogen splitting vs. proton reduction selectivity emphasizes the role of hydrogen bonding of the conjugate base with the protonated intermediates and provides guidelines for nitrogen fixation.

Introduction

Homogeneous N2 fixation under ambient conditions has made remarkable progress over the past 15 years.1 Nishibayashi and co-workers recently obtained over 4000 equiv. of NH3 with the proton coupled electron transfer (PCET) reagent H2O/Sml2 as H+/e− sources and a molecular Mo pincer catalyst.2 Accordingly, nitrogen reduction (NR) via electrochemically or light-driven PCET with related systems has attracted a lot of attention.3,4 Lindley et al. estimated a suitable overpotential window of 1–1.5 V for selective NR (in MeCN) prior to competing hydrogen reduction (HR) at a glassy carbon cathode.5 However, besides the thermochromical framework, mechanistic models that account for NR vs. HR selectivities of molecular catalysts are generally poorly developed.

Several M(N2H6) intermediates relevant to N2 fixation (Scheme 1) exhibit low N–H bond dissociation free energies (BDFEs) below that of free H2 (BDFE(H2, gas) = 97.2 kcal mol−1) as possible branching points into HR.6,7 Computational evaluation of NR vs. HR selectivities for a series of Fe catalysts pointed at bimolecular H2 loss from species with low N–H BDFEs.8,9 Attempts to stabilize such Fe(NxHx) species by hydrogen bonding with pendant bases so far resulted in shutdown of catalysis.10 But, in fact, such secondary interactions might also be relevant for Nishibayashi’s catalyst as indicated by selectivities obtained with 2,6-lutidinium acids ([LutH]+[X−]) as the proton source. These strongly depend on the X− counter anion: NH3/H2 (X−) = 7.0 (Cl−), 0.9 (OTf−), and 0.14 (BAr4−).11

In this contribution, we address the role of hydrogen bonding for the selectivity of proton induced N2 splitting into molecular nitrides vs. proton reduction. N2 splitting has evolved as an entry into N2 functionalization for a wide variety of metals12 and was proposed as the key step in N2 fixation with Mo pincer catalysts.2,13 Cleavage of Cummins’ seminal complex 1 (Fig. 1) was attributed to the {πη2, πη2, πη2, πη2, πη2} configuration of the Mo2N2-core, which enables population of

Scheme 1  Transition metal species relevant to N2 fixation with a low BDFE(Nx−Hx).7
formation from N₂ is surprisingly rare.²⁰ We here report tungsten mediated N₂ splitting that competes with proton reduction upon protonation of a {W₂N₂} pincer complex. Our results provide evidence for the significance of hydrogen bonding for the reaction selectivity.

Results and discussion

Synthesis of the [(N₂)(WCl(PNP))]₃⁺⁺ (n = 0–2) redox series

The reaction of WCl₄ with HPNP in the presence of NEt₃ gives the pincer complex [WCl₃(PNP)] (5) in yields of up to 60%. In the absence of a signal in the ³¹P{¹H} NMR spectrum, the paramagnetically shifted ¹H NMR signals and the solution magnetic moment derived by Evans’ method (μₑff = 2.8 ± 0.1 μμ) are in line with a d² high-spin (S = 1) configuration. The molecular structure obtained by X-ray diffraction closely resembles previously reported compounds [MCl₃(PNP)] (M = Re and Mo).¹⁸,¹⁹

Reduction of 5 with Na/Hg (2 equiv.) under N₂ (1 atm) in THF gives the green, N₂-bridged dinuclear complex [(N₂)W₂Cl₂(PNP)] (6) in up to 66% isolated yield (Scheme 3). In the solid state (Fig. 2) 6 is isosctructural with the molybdenum analogue 4, regarding the N₂ binding mode, the approximate C₂ symmetry due to mutually twisted [WCl(PNP)]-fragments (C11'-W1-W1#-Cl1#’: 89.59°/92.27°), and the distorted square-pyramidal metal coordination (τ = 0.35).²¹ The short W–N₂ bond (1.78(2)/1.82(4) Å) indicates multiple bonding character. In turn, the N–N bond (1.33(4)/1.27(8) Å) is at the higher end for

Table 1  Comparison of the spectroscopic and structural features of Cummins’ Mo–N₂ dimer redox series (Ar = C₆H₅–3,5-Me₂) with square-pyramidal pincer complexes (M = Re,²⁰ Mo,¹⁸ or W, * computed value)

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<th>1</th>
<th>2²⁺</th>
<th>3 (M = Re)</th>
<th>4 (M = Mo)</th>
<th>6 (M = W)</th>
<th>7⁺ (M = W)</th>
<th>8²⁺ (M = W)</th>
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<td>0</td>
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<td>+1</td>
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<tr>
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<tr>
<td>d(NN) [Å]</td>
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<td>1.239(4)</td>
<td>1.265(5)</td>
<td>1.202(10)</td>
<td>1.258(9)</td>
<td>1.33(4)/1.27(8)</td>
<td>1.277(5)</td>
</tr>
<tr>
<td>ν(NN) [cm⁻¹]</td>
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<td>1503</td>
<td>1349</td>
<td>1771*</td>
<td>1343</td>
<td>1392</td>
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<td>1</td>
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</tr>
</tbody>
</table>

Fig. 1 Qualitative molecular orbital schemes for 1, 2²⁺, 3 and 4, illustrating the isolobal relationship of 1 (π¹⁰)/3 (π¹⁰) and 2²⁺ (π⁰)/4 (π⁰), respectively.
N₂-bridged ditungsten complexes. The two ³¹P{¹H} NMR signals (δₚ = 92.9, 87.8 ppm) with large trans-coupling (Jₚᵥ = 147 Hz), the singlet ¹⁵N NMR resonance (δₕ = 31.1 ppm), and the ¹H NMR signature of 6 support a C₂ symmetric structure also in solution on the NMR timescale.

The N₂ stretching vibration of 6 was assigned to the Raman signal at 1392 cm⁻¹ (δₑₓₑ = 457 nm, THF solution; 15N₂ isotopologue: 1347 cm⁻¹) supporting strong N₂-activation with a formal N-N bond order below the double bonding character (trans-diines: 1329 cm⁻¹). The closed-shell ground state and degree of N₂ activation are in line with the covalent bonding picture described in Fig. 1. The {π*δ} configuration of the W₂N₂ core can be rationalized to arise from two low-spin WII ions. The twisted conformation enables strong back bonding of each metal ion with one π*-MO of the N₂ bridge, respectively, resulting in net transfer of approximately two electrons as judged from the Raman data. This picture is corroborated by DFT computations, which confirm the {π*δ} configuration of the W₂N₂ core, analogous to the Mo analogue 4 and Cummins’ 2+.

The blue-shifted N₂ stretching vibration of 6 vs. 4 (δₑₓₑ = 49 cm⁻¹; Table 1) indicates slightly reduced back-bonding by the 5d metal.

The redox chemistry of 6 was examined to probe the electronic structure model. Cyclic voltammetry (CV) in THF shows no reduction feature down to -2.9 V (vs. FeCp₂/FcFeCp₂). In contrast, two reversible oxidation waves (E⁰₁ = -1.39 V; E⁰₂ = -0.91 V) are observed. Both redox events are cathodically shifted by 250 mV with respect to the Mo analogue 4, supporting metal centered oxidation. The oxidation products [(N₂)WCl(PNP)]⁺ (7+) and [(N₂)WCl(PNP)]²⁺ (8⁺) could be isolated in yields beyond 80% upon chemical oxidation of 6 with one and two equivalents of silver salts, respectively (Scheme 3).

Stabilization of 8⁺ requires a weakly coordinating anion, which was introduced with Ag[Al(OClF₅)₃]₁ as the oxidant.

In the solid state, 7⁺ and 8⁺ resemble the twisted conformation found for 6 (Fig. 2). Distinctly different bond lengths around the two tungsten ions of the mixed-valent complex 7⁺ indicate valence localization, which is further supported in solution by the large comproportionation constant (K = 10⁸) and the X-band EPR spectrum at r.t. The isotropic signal (gₑₓₑ = 1.93) of the low-spin (S = 1/2) complex exhibits hyperfine interaction (HFI) with only one tungsten (Å¹¹W = 220 MHz) and two phosphorous nuclei (Å¹¹P = 56 MHz), respectively. HFIs with the N₂-bridge are not found and the ¹⁴N₂- and ¹⁵N₂-isotopologues give identical spectra, further supporting metal centered oxidation. In fact, the degree of N₂ activation is almost invariant within the redox series 6/7+/8⁺ as judged from the invariance of the N-N stretching vibrations and the N-N bond lengths of the W₂N₂ cores (Table 1). Notably, the ¹H NMR spectrum of 7⁺ features four signals assignable to 8B groups, in agreement with the averaged C₂ symmetry and therefore valence delocalization on the slow NMR timescale.

The double oxidation product 8²⁺ exhibits paramagnetically shifted, yet relatively sharp ¹H NMR signals. Magnetic characterization by SQUID magnetometry reveals a λ₊ₜ product of about 0.6 cm³ mol⁻¹ K⁻¹ at r.t., which gradually drops to 0 at about 20 K. The data can be fitted to a model with two weakly antiferromagnetically coupled (J = -59 cm⁻¹) low-spin (S = 1/2) ions. The g-value (gₑₓₑ = 1.90) indicates an orbital contribution in the typical range for W⁷⁺ complexes with multiply bound hard ligands, such as oxo or nitrido complexes.

Characterization of the redox series 6/7+/8⁺ supports the electronic structure picture with {π*δ}/(π*δ)/{π*δ} configurations for the W₂II/W₂I (6), W₂II/W₂I (7⁺) and W₂II/W₂I (8⁺) complexes, respectively (Fig. 1 and Table 1). The spin orbitals of 7⁺ and 8⁺ are orthogonal to the W₂N₂ core resulting in weak...
mutual coupling via the N$_2$ bridge ($\nu$(82+) = −59 cm$^{-1}$). In consequence, all three complexes of the redox series exhibit strong back bonding to the N$_2$ bridge with only weakly affected degrees of N$_2$ activation. These interpretations are corroborated by DFT (ESI†). Doublet \{π$^2\delta_1\delta_1\}^2$ (7′) and open-shell singlet \{π$^2\delta_1\delta_2\}^2$ (82+) ground states, respectively, were computed with a low lying triplet state for 82+ due to weak antiferromagnetic coupling of the metal centered spins ($J_{DFT}$ = −184 cm$^{-1}$).

**Protonation induced N$_2$ splitting vs. proton reduction**

N$_2$ splitting of 6 into the nitride [W(N)Cl(HPNP)]OTf (9OTf, Scheme 4) as the only detectable tungsten species (NMR/EPR spectroscopy, HR-ESI-MS) was achieved upon adding 2 equiv. of triflic acid at −78 °C and gradual warming to r.t. Complex 9OTf could be isolated in over 60% yield and was fully characterized. The tungsten(v) nitride is NMR silent and features an isotropic signal ($g_{av}$ = 1.93) in the X-band EPR spectrum (THF, r.t.) with HFIs with the tungsten and phosphorous nuclei ($\Delta(I^{19}W) = 220$ MHz; $\Delta(I^{31}P) = 56$ MHz). The W≡N stretching vibration is found in the IR spectrum at 1058 cm$^{-1}$ ($\nu$(W≡N); $\Delta\nu$ = 29 cm$^{-1}$). In the solid state (Fig. 3), 9 is isostructural with the molybdenum analogue,\textsuperscript{19} featuring square-pyramidally coordinated tungsten with the nitride ligand in the apical site. Hydrogen bonding of the amine proton with the triphenylmonocation is indicated by the short NH·O distance (2.03(3) Å). The W≡N bond length (1.679(2) Å) is in the typical range found for the related tungsten nitrides.\textsuperscript{3,4,7,26}

In contrast to the Mo analogue 4 (Scheme 2), the selectivity of protonation induced N$_2$ splitting strongly varies with the reaction conditions. The addition of HOTf (2 equiv.) to 6 at r.t. results in low nitride yields and substantial amounts of the oxidation products 7+ and 82+. Furthermore, 2 equiv. of strong acids with weakly coordinating anions, such as [H(OEt)$_2$]$_3$[Al(OC(CF$_3$)$_3$)$_3$] and [H(OEt)$_2$][BArF$_{24}$][BArF$_{24}$] (BArF$^-_{24}$ = B(C$_6$H$_3$-3,5-B$_2$H$_4$)$_2$), exclusively gave dicaticionic 82+ both at low (−70 °C) and ambient temperatures (Scheme 4). Concomitant H$_2$ evolution was confirmed by gas chromatography. Reaction of 6 at r.t. with 1 equiv. of these and other acids (HOTf, (2,6-lutidinium) OTf, [HNEt$_3$][BArF$_{24}$], [H(OEt)$_2$][BArF$_{24}$], and [H(OEt)$_2$] [Al(OC(CF$_3$)$_3$)$_3$]) selectively gives the oxidation product 7+ in all cases.

![Scheme 4](image_url)  
Scheme 4  Protonation of 6 with 2 equiv. of different acids.

Next, the influence of the acid counterion on the selectivity was probed. Upon protonation with [HNEt$_3$][BArF$_{24}$] (2 equiv.), 7+ was found exclusively (Scheme 5). The second oxidation is hampered by the higher pK$_a$ of this acid vs. HOTf, which prevents protonation of the monocaticionic product. Importantly, this selectivity changes with [HNEt$_3$]OTf (2 equiv.): in this case, 7+ is obtained in spectroscopic yields of up to only 30%. In situ HR-ESI-MS examination indicates that nitride 9 is formed as the only other product. This observation is reminiscent of acid dependent selectivities reported by Nishibayashi for catalytic nitrogen fixation (see above).\textsuperscript{11} For this reason, [HNEt$_3$]Cl (2 equiv.) was also used. Unfortunately, sluggish mixtures of products were obtained, including substantial amounts of trichloride 5. In the next sections, experimental and computational mechanistic examinations with only [HNEt$_3$]X (X$^-$ = BAr$^{F_{24}}$, OT$^-$) are therefore reported.

**Mechanistic examinations**

Stoichiometric protonation at low temperatures was carried out to obtain spectroscopic information about intermediates. With 1 equiv. of HOTf at low $T$ (−35 °C), the NMR data are in agreement with pincer protonation to diamagnetic dinuclear...
C1-symmetric $[\text{HPNP}][\text{ClW(μ-N2)}][\text{WCl(PNP)}][\text{OTf}]$ (10OTf), analogous to the respective Mo system (Scheme 6).

Notably, immediate formation of the oxidation product $7^+$ was observed with $[\text{H(OEt2)}][\text{BARF}_{24}]$, even at temperatures down to $-75^\circ\text{C}$. The enhanced stability of 10OTf suggests an interaction of the immediate protonation product with the trialkylamine. Contact-ion pair formation is confirmed by $^{19}\text{F}$ and $^1\text{H}$ DOSY NMR spectroscopy at $-35^\circ\text{C}$. The diffusion coefficient of the trialkylamine in 10OTf ($D = 2.29 \times 10^{-6}$ cm$^2$ s$^{-1}$) is in the same range as that of the cation ($D = 2.18-2.14 \times 10^{-6}$ cm$^2$ s$^{-1}$) and significantly reduced compared to free triflic acid ($D = 5.11 \times 10^{-6}$ cm$^2$ s$^{-1}$). We tentatively attribute the solution ion-pairing to hydrogen bonding of the trialkylamine with the pincer N–H proton, as found in the solid state for 9OTf (Fig. 3).

Protonation of 6 with 2 equiv. of HOTf at low temperatures in THF is associated with a color change from green to yellow. The absence of a signal in the $^{31}\text{P}$($^1\text{H}$) NMR spectrum and the disappearance of all $^1\text{H}$ NMR signals, as expected for selective $\text{N}_2$-splitting into the pale, NMR silent nitride product $9^+$, was used as the acid, which selectively gives a convenient timescale even under pseudo first-order conditions. Additional of the acid to 6 in THF leads to an immediate drop of absorbance without significant change of the absorption maxima, suggesting only small changes in the electronic structure. The acid concentration dependence of the absorbance at 607 nm for the presumable product, $[\text{HNEt}_3][\text{BARF}_{24}]$, was estimated with Evans’ method at $-60^\circ\text{C}$ ($\mu_{eff} = 4.7 \mu_0$), i.e., close to the spin-only value for a quintet ground state ($4.9 \mu_0$). 

Mechanistic information about proton reduction was obtained from kinetic studies. For this purpose, $[\text{HNEt}_3][\text{BARF}_{24}]$ was used as the acid, which selectively gives $7^+$ at r.t. within a convenient timescale even under pseudo first-order conditions. Addition of the acid to 6 in THF leads to an immediate drop of absorbance without significant change of the absorption maxima, suggesting only small changes in the electronic structure. The acid concentration dependence of the absorbance for estimating the equilibrium constant and forward rate of the initial protonation of 6 ($K_1 = 1592 \pm 578$ M$^{-1}$, $k_1 = 163 \pm 47$ M$^{-1}$ s$^{-1}$; Scheme 7 and Fig. S25 and S26 in the ESI†). This step is followed by a much slower, monoeponential decay, which was monitored over 5 h (Fig. 4, left). Under pseudo first order conditions in acid ($c(\text{HNEt}_3)\approx c(\text{6}) = 10$–25), the rate constant ($k_{obs(2)}$) linearly depends on the acid concentration (Fig. 4, right), which is in agreement with a slow, irreversible second protonation after the initial, fast pre-equilibrium $K_1$. However, the non-zero intercept indicates the presence of at least one competitive pathway at a low acid concentration. The rate constant $k_{obs(2)}$ for the formation of $7^+$ was therefore expressed as eqn (1) which results from the minimum kinetic model outlined in Scheme 7:

$$k_{obs(2)} = \frac{k_2K_1[H^+]^2}{1+K_1[H^+]} + k_{obs}$$

The first term accounts for the initial protonation of 6 to give $10^+$, followed by irreversible H$_2$ release from acid and 10$^+$. Rapid, subsequent comproportionation of the resulting 8$^+$ with 6 to 2 × 7$^+$ is in line with the electrochemical results ($K_e = 10^+$, see above). The second term in eqn (1) is ascribed to bimolecular decay of 10$^+$ as an alternative path at low acid concentrations. The rate constant $k_3 = 0.018 \pm 0.001$ M$^{-1}$ s$^{-1}$ was derived from fitting the experimental data to eqn (1) (with preserved $K_1$) under pseudo first order conditions in acid (10–25 equiv.). The rate constant $k_3 = 0.4$ M$^{-1}$ s$^{-1}$ for the bimolecular path at low acid concentrations was obtained from the initial rate of the reaction of 6 and an equimolar amount of $[\text{HNEt}_3][\text{BARF}_{24}]$. 

Kinetic analysis suggests two pathways for H$_2$ formation which both go through the spectroscopically characterized common intermediate 10$^+$ (as 10OTf). Path B (Scheme 7) explains the decay of 10$^+$ even in the absence of the acid and reflects a bimolecular H$_2$ formation route as proposed by Matson and Peters for an iron diazenide N$_2$-fixation intermediate. However, path A is predominant with excess acid. Besides these routes for hydrogen evolution, splitting of the N$_2$ bridge is observed in the presence of triflate as the counteranion and is even selective at

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**Scheme 6** Oxidation of 6 with 1 equiv. of acid at different temperatures.

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**Scheme 7** Proposed mechanistic pathways for proton reduction at high (Path A) and low (Path B) acid concentrations.

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**Fig. 4** Left: plot of the absorbance at 607 nm vs. time for different concentrations of $[\text{HNEt}_3]^+$. Results from fitting to the rate law are indicated by red lines. Right: plot of $k_{obs(2)}$ vs. $[\text{HNEt}_3]^+$. 

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lower temperatures. These effects are rationalized computationally in the next section.

Computational examinations

Protonation with \([\text{NET}_3\text{H}][\text{BARF}_{24}^+]\) was first examined computationally with trimethylammonium as the model acid (Scheme 8). Two different sites, a metal ion and a pincer nitrogen atom, respectively, were considered for the first protonation step. A hydride product \([\text{PNP}]\text{W}[\text{H}]\text{Cl}[\mu-\text{N}_2]\text{WCl}[\text{PNP}]^-\) (12+) adopts an electronic singlet \((S = 0)\) ground state and was found to be the global protonation minimum at \(\Delta G_{298}^\ddagger = -4.7\ \text{kcal mol}^{-1}\) below 6 and \([\text{NMe}_3\text{H}]^+\). Hence, the model computation is in excellent agreement with the experimental equilibrium constant \(K_1\). The computed structure of 12+ features a bridging hydride between the metal ion and a pincer phosphorous atom. A similar structure was previously found experimentally by Schrock and co-workers for the protonation of a PCP molybdenum(v) nitride by \([\text{NEt}_3\text{H}]\)\([\text{BArF}_4^-]\). All efforts to experimentally verify hydride intermediates like 12+ were unfortunately unsuccessful. However, pincer protonation to 10+ is only slightly less exergonic \(\Delta G_{298}^\ddagger = -2.9\ \text{kcal mol}^{-1}\). Importantly, this state is further stabilized upon use of \([\text{NET}_3\text{H}]\)\([\text{BARF}_{24}^+]\) as the acid due to hydrogen bonding of the pincer amine moiety with the triazine anion by \(\Delta G_{298}^\ddagger = -2.1\ \text{kcal mol}^{-1}\). In contrast, the hydride ligand is not involved in hydrogen bonding, rendering 10OTf \(\Delta G_{298}^\ddagger = -5.0\ \text{kcal mol}^{-1}\) the global minimum of the first protonation in the presence of triazine. Overall, the metal and pincer protonation products 12+ and 10+ (and 10OTf in the presence of triflate) should be in rapid equilibrium under these conditions, which is slightly shifted towards pincer protonation by hydrogen bonding with the counteranion. Notably, hydrogen bonding with the conjugate base NMe3 was not observed, presumably for steric reasons.

Starting from the amine/hydride equilibrium, the second protonation with \([\text{NMe}_3\text{H}]^+\) can ultimately lead to hydrogen evolution or \(N_2\) splitting, respectively. The formation of \(H_2\) and dicaticonic 82+, which represents Path A (Scheme 7), was computed to be exergonic by \(\Delta G_{298}^\ddagger = -12.8\ \text{kcal mol}^{-1}\) with respect to 6. The most reasonable pathway (Scheme 8, right branch) proceeds via hydride protonation of 12+ leading to the dihydrogen intermediate \([\text{PNP}]\text{W}[\text{H}]\text{Cl}[\mu-\text{N}_2]\text{WCl}[\text{PNP}]^-\) (132+), which is unstable and readily releases \(H_2\) without barriers. While the transition state that leads from 12+ to 132+ could not be reliably located due to the flat potential energy profile of protonation, the free energy of 132+ \(\Delta G_{298}^\ddagger = +19.7\ \text{kcal mol}^{-1}\) with respect to 12+) was used as an estimate for the kinetic barrier of hydride protonolysis. Notably, this value is in excellent agreement with the experimentally derived barrier for Path A \((k_2 = 0.018\ \text{M}^{-1}\ \text{s}^{-1}; \Delta G_{298}^\ddagger = 19\ \text{kcal mol}^{-1})\).

Alternatively, splitting of the dinitrogen bridge (Scheme 8, left branch) was computed to proceed via protonation of the second pincer nitrogen. In the absence of triflate, \([\text{N}_2][\text{WCl}[\text{H}][\text{PNP}]]_{22}^{2+}\) (112+) was located at \(\Delta G_{298}^\ddagger = +5.0\ \text{kcal mol}^{-1}\) vs. 6 \(\Delta G_{298}^\ddagger = +9.7\ \text{kcal mol}^{-1}\) vs. the global first protonation minimum 12+) adopting an electronic quartet \((S = 2)\) ground state in accordance with the experimental findings for 11OTf2-. From there, N2 cleavage into the nitrides \(9^+\) was computed to be strongly exergonic \(\Delta G_{298}^\ddagger = -49.7\ \text{kcal mol}^{-1}\) with a kinetic barrier \(\Delta G_{298}^\ddagger = 21.7\ \text{kcal mol}^{-1}\) that is comparable to the experimentally derived barriers for \([\text{N}_2][\text{MoCl}[\text{H}][\text{PNP}]]_{22}^{2+}\) \(\Delta G_{298}^\ddagger = 19.5\ \text{kcal mol}^{-1}\) and \([\text{N}_2][\text{ReCl}[\text{PNP}]]_{22}^{2+}\) \(\Delta G_{298}^\ddagger = 19.8\ \text{kcal mol}^{-1}\), respectively. For the tungsten system, this gives

![Scheme 8](Image)

Scheme 8 Computed energy profile for protonation induced \(N_2\) splitting (left branch) and hydrogen evolution via Path A (right branch) via double protonation of the dinitrogen complex 6 at room temperature in the absence (solid line) and presence (dashed line) of triflate as the counteranion.
rise to an overall effective barrier for protonation induced \( \text{N}_2 \) splitting from the most stable monoprotonation intermediate, hydride \( \text{1}^{2+} \), of \( \Delta G_{298}^{\ddagger} = 31.4 \text{ kcal mol}^{-1} \). This value is considerably higher than the estimate for the hydrogen evolution pathway (\( \Delta G_{298}^{\ddagger} = +11.5 \text{ kcal mol}^{-1} \)), which is in line with selective proton reduction with [NEt\(_3\)H][\text{BARF}^{14+}] as the acid.

Importantly, the relative energetics of these two reaction channels are perturbed in the presence of triflate as the counterion. As was found for the first pincer protonation (see above), triflate hydrogen bonding stabilizes the pincer diprotonation product \( \text{11}^{\text{OTf}} \) by \(-8.8 \text{ kcal mol}^{-1} \). Consequently, the estimated effective barrier for hydrogen evolution (\( \Delta G_{298}^{\ddagger} = 20.2 \text{ kcal mol}^{-1} \)) vs. the global first protonation minimum in the presence of triflate \( \text{10}^{\text{OTf}} \) is slightly raised. On the other hand, the \( \text{N}_2 \) splitting pathway (\( \Delta G_{298}^{\ddagger} = 21.5 \text{ kcal mol}^{-1} \)) vs. \( \text{10}^{\text{OTf}} \) is almost isoeenergetic, in full agreement with the experimental findings. The triflate induced effect on selectivity is therefore attributed to Curtin–Hammett controlled reactivity wherein \( \text{N–H} \) hydrogen bonding to the counterion modifies the energetics of the protonation pre-equilibria.

A similar picture evolves for the reaction with triflic acid (see the ESI, Scheme S1†). However, the potential energy of protonation is augmented by the higher driving force with the stronger acid (\( pK_A^\beta (\text{Et}_3\text{NH}^-) = pK_A^\beta (\text{HOTf}) = 4.7 \)).28 This affects the selectivity as the effective barrier for the \( \text{N}_2 \) splitting branch versus hydrogen evolution is close in energy. Furthermore, all rate determining states are below the starting point \( \text{6} \). In consequence, under these conditions (HOTf as the acid at r.t.), Curtin–Hammett conditions do not apply resulting in the experimentally observed low selectivity.

Reduction of the temperature to \(-80 \text{ °C}\) further perturbs the relative energetics of the two reaction pathways with HOTf. The computed amine (\( \Delta G_{93}^{\ddagger} (\text{10}^{\text{OTf}}) = 15.1 \text{ kcal mol}^{-1} \)) vs. hydride (\( \Delta G_{93}^{\ddagger} (\text{12}^{+}) = -10.3 \text{ kcal mol}^{-1} \)) equilibrium is even more shifted towards the amine due to the lower entropic penalty for hydrogen bonding at low \( T \). The negligible population of the hydride tautomer in agreement with the exclusive experimental observation of \( \text{10}^{\text{OTf}} \) and \( \text{11}^{\text{OTf}} \) upon single and double protonation with HOTf at \(-80 \text{ °C}\). From \( \text{11}^{\text{OTf}} \), the dihydrogen complex \( \text{13}^{+} \) (\( \Delta G_{93}^{\ddagger} (\text{13}^{+}) - \Delta G_{93}^{\ddagger} (\text{11}^{\text{OTf}}) = +27.7 \text{ kcal mol}^{-1} \)) is much higher in free energy than the barrier for \( \text{N}_2 \) splitting (\( \Delta G_{93}^{\ddagger} (\text{k} = 19.9 \text{ kcal mol}^{-1} \)), in line with selective \( \text{N}_2 \) splitting upon double protonation with HOTf at \(-80 \text{ °C} \) and slow warming.

**Concluding remarks**

In summary, an anion effect on the selectivity of proton induced dinitrogen splitting (NR) vs. hydrogen evolution (HR) at the \( \text{N}_2 \) bridged ditungsten complex \( \text{6} \) was demonstrated and rationalized. Our spectroscopic, kinetic and computational studies suggest some guidelines to improve NR over HR yields:

(a) Nitrogen vs. metal protonation offers separate reaction channels with a proposed hydride isomer leading to hydrogen evolution analogous to the highly active Mo-oxo poly(pyridyl) HR catalysts.29 The tautomerisation equilibrium can be offset by hydrogen bonding with protic \( \text{N–H} \) hydrogen atoms favoring the use of an acid [BH]\(^+\)X\(^-\) where the anion X\(^-\) is prone to form H-bonds for high NR selectivity.

(b) Protonation under Curtin–Hammett control with weak acids can become irreversible with strong acids. Hence, the \( pK_A \) of the acid can have a decisive kinetic effect on the selectivity.

(c) Lower temperatures favour hydrogen bonding interactions due to the reduced entropic penalty as a strategy for increased NR yields.

Besides the immediate application to the current system, these findings might be considered as a model reaction for nitrogen fixation schemes. The studies of Peters and of Nishibayashi have emphasized the importance of proton coupled electron transfer for \( \text{N}_2 \) fixation under ambient conditions. Our kinetic model might therefore offer some general strategies regarding the choice of acid to improve NR selectivities with respect to unproductive proton reduction.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

† An alternative pathway via reduction of \( \text{10}^+ \) with \( \text{6} \) is less likely based on the derived rate constant (\( k_1 = 0.12 \text{ M}^{-1} \text{s}^{-1} \)), which is considerably smaller than \( k_2 \).

§ A transition state for the direct protonation of \( \text{12}^+ \) with [HNMe\(_3\)]\(^+\) at the hydride ligand was located at \( 25.4 \text{ kcal mol}^{-1} \) above \( \text{6} \) and two equivalents of [HNMe\(_3\)]\(^+\).

However, this activation free energy is considerably higher than the experimentally determined value (\( \Delta G_{\text{xaa}}^{\ddagger} = 19 \text{ kcal mol}^{-1} \)). It is not clear if this deviation can be attributed to the computational truncation of the acid or to a lower competing pathway. We therefore prefer to use the experimental value for the discussion of the selectivity. See also the ESI for further discussion.†

   (c) K. C. MacLeod and P. Holland, *Nat. Chem.*, 2013, 5, 559–565;


