

Rapid, Reversible Heterolytic Cleavage of Bound H₂

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Supporting Information

ABSTRACT: Heterolytic cleavage of dihydrogen into a proton and a hydride ion is a fundamentally important step in many reactions, including the oxidation of hydrogen by hydrogenase enzymes and ionic hydrogenation of organic compounds. We report the facile, *reversible* heterolytic cleavage of H₂ in a manganese complex bearing a pendant amine, leading to the formation of a manganese hydride and a protonated amine that undergo H⁺/H⁻ exchange at an estimated rate of >10⁷ s⁻¹ at 25 °C.

T he H–H bond of dihydrogen is the simplest chemical bond and has served as the prototypical bond for fundamental experimental and theoretical studies. The formation and cleavage of H₂ can occur homolytically (H·/H·) or heterolytically (H⁺/H⁻) and is an essential step in many reactions, including the production of H₂,¹ the oxidation of H₂,² and catalytic hydrogenation of a diverse range of unsaturated bonds.³ In polar environments, typical of enzymatic or electrochemical reactions, the heterolytic bond strength for H–H cleavage⁴ is lower than the homolytic bond strength, favoring heterolytic scission. Bifunctional interactions that facilitate the heterolysis of H₂ (Figure 1) are important to



Figure 1. Intramolecular deprotonation of bound H₂.

the function of many types of hydrogenation catalysts and the family of hydrogenase enzymes.^{5,6} A detailed understanding of the heterolysis of a nonpolar bond would greatly inform the design of systems based on heterolytic activation. Here we report an extremely facile, *reversible* heterolytic cleavage of the H–H bond in a Mn complex, wherein the proton and hydride ion undergo exchange through an energetically accessible $Mn(\eta^2-H_2)^+$ intermediate at an estimated rate of >10⁷ s⁻¹ at 25 °C.

To mimic a salient feature in the active sites of hydrogenase enzymes,⁷ pendant amine bases have been incorporated into families of Ni, Co, and Fe complexes, and their electrochemical behavior under acidic and basic conditions has been studied. This has led to the development of catalysts for H_2 production and oxidation using inexpensive, abundant transition metals rather than precious metals such as platinum.⁸ Exploiting a large variety of metal complexes with varying coordination

environments and oxidation states allows for multiple means of controlling the catalytic rate and overpotential. We previously studied cationic Mn(I) complexes containing pendant amines and found that the stable Mn(η^2 -H₂)⁺ adducts showed no evidence for heterolytic cleavage of H₂.⁹ Reasoning that the acidity of the H₂ ligand in our previous complexes was insufficient to lead to heterolysis, we found in the present work that incorporation of an electron-deficient diphosphine ligand into a new Mn complex (Figure 2) increased the electrophilicity at Mn, facilitating rapid, reversible heterolytic cleavage of H₂.

The cationic complex 1 (Figure 2) was prepared by halide abstraction from $(P_2^{Ph}N_2^{Bn})Mn(Br)(CO)(bppm)$ [bppm =



Figure 2. Syntheses of $[(\kappa^3 - P_2^{\text{Ph}} N_2^{\text{Pn}}) \text{Mn}(\text{CO})(\text{bppm})][\text{BAr}_4^{\text{F}}]$ (1) and $[(P_2^{\text{Ph}} N_2^{\text{Bn}} \text{ H}) \text{MnH}(\text{CO})(\text{bppm})][\text{BAr}_4^{\text{F}}]$ (2) and the truncated solid-state structure of the cation of 2 (-123 °C, 50% probability ellipsoids).

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Figure 3. Selected regions of (A) ¹H (with deconvolution) and (B) ¹H{³¹P} NMR spectra of 2; (C) ¹H{³¹P}, (D, top) ¹⁵N{¹H}, and (D, bottom) ¹⁵N NMR spectra of $2[^{15}N]$; and (E) ²H and (F) ¹H NMR spectra of 2-(H/D) from -20 to -70 °C.

 $(PAr_{2}^{F})_{2}CH_{2}$; $Ar^{F} = 3,5$ -bis(trifluoromethyl)phenyl] through treatment with excess NaBAr₄ in fluorobenzene. While similar Mn cations previously prepared by Kubas and co-workers are intensely blue,¹⁰ **1** is red-orange as a result of coordination of one of the pendant amines to the Mn center [Figure S1 in the Supporting Information (SI). The ³¹P NMR resonance for the P₂N₂ ligand of **1** was broad at room temperature (Figure S2B), consistent with dynamic behavior related to reversible dissociation of the coordinated pendant amine.

Addition of H₂ (1 atm) to 1 in PhF or CD₂Cl₂ at -20 °C resulted in a color change from red to yellow and the formation of a single new product (see the ³¹P NMR spectrum in Figure S3). Yellow-orange crystals of 2 were grown from CH₂Cl₂ solutions under H₂, and the solid-state molecular structure determined by X-ray diffraction (Figure 2) is consistent with a static structure containing Mn–H and N–H bonds resulting from heterolytic cleavage of H₂.¹¹

Spectral studies of 2 in solution indicated dynamic behavior. Besides the expected resonances from ligand protons, the ¹H NMR spectrum of **2** in CD_2Cl_2 exhibited a pseudopentet (J_{PH} \approx 15 Hz, 2H) at 2.55 ppm that collapsed to a broad singlet upon broadband ³¹P decoupling (Figure 3A, B). The modest ³¹P coupling [not observed in similar $Mn(\eta^2-H_2)^+$ complexes^{9,10}] and the unusual chemical shift are inconsistent with those of Mn(η^2 -H₂)⁺ (typically -2 to -5 ppm)⁹ or a static structure containing a Mn-H bond (typically -4.5 to -6 ppm)¹¹ and a N–H bond in the protonated P_2N_2 ligand (14 to 7 ppm). When D₂ was used to produce 2-(D/D), the ¹H NMR spectrum was identical to that of 2 except for the absence of the peak at 2.55 ppm, and the ²H NMR spectrum contained a singlet at 2.5 ppm (Figure S4). The existence of a single ¹H NMR resonance attributable to the Mn-H and N-H positions indicated that those moieties are in rapid exchange, and further isotopic labeling studies supported this conclusion.

In the ¹H NMR spectrum of the ¹⁵N-labeled analogue $2[^{15}N]$ prepared from $1[^{15}N]$ and H_2 , the Mn-H/N-H resonance appeared as a doublet of pentets that collapsed to a doublet upon broadband ³¹P decoupling ($J_{NH} = 37$ Hz; Figure 3C). The ¹⁵N nucleus coupled to the Mn-H/N-H resonance (assigned by ¹H,¹⁵N-HSQCAD) appeared as a triplet of triplets in the ¹⁵N NMR spectrum ($J_{NP} = 7.4$ Hz, $J_{NH} = 37$ Hz; Figure 3D), indicating coupling between this ¹⁵N nucleus and *two* dynamically equivalent protons. The magnitude of J_{NH} is

consistent with rapid proton-hydride exchange that results in the observation of an average coupling constant for a "normal" ${}^{1}J_{\rm NH}$ (~70 Hz)¹² from the protonated amine and negligible ¹⁵N coupling ($J_{\rm NH} \approx 0$ Hz) to the hydride ligand. Similarly, the magnitude of $J_{\rm PH}$ is approximately half of the value expected for manganese hydrides in this structural family (${}^{2}J_{\rm PH}$ = 15 Hz observed vs 30–40 Hz expected).¹¹

Addition of HD to a CH_2Cl_2 solution of 1 at -20 °C resulted in the observation of an ¹H NMR spectrum containing resonances identical to those of 2 except for the absence of a peak near 2.5 ppm. Instead, a signal integrating to one proton was observed at -2.78 ppm that appeared as a pseudopentet $(J_{\rm PH} = 28 \text{ Hz})$ and collapsed to a singlet upon broadband ³¹P decoupling. The ²H NMR spectrum of the same sample revealed only a resonance at +7.8 ppm. In the variabletemperature ²H and ¹H NMR spectra of 2-(H/D) from -20 to -70 °C (Figure 3E,F), both the ¹H and ²H chemical shifts showed a strong temperature dependence, linearly shifting by >1 ppm in opposite directions (upfield and downfield, respectively, with decreasing temperature) over a 50 °C range. The average of these chemical shifts in the ¹H and ²H NMR spectra was 2.5 ppm, consistent with a dynamic process involving rapid exchange of H and D between the amine and metal sites, with a preference for D at the amine and the H at the metal.¹³ Although the ²H signal became too broad below -70 °C to allow the chemical shift to be quantified reliably, the ¹H signal continued to shift consistently upfield, reaching -4.32ppm at a temperature of -94 °C (Figure S5).

The assignment of the resonance at 2.55 ppm in the ¹H NMR spectrum of **2** to rapidly exchanging proton and hydride resonances is thus consistent with the observed average chemical shift, the magnitudes of ${}^{1}J_{\rm NH}$ and ${}^{2}J_{\rm PH}$, and the coupling of two hydrogen atoms to the corresponding ¹⁵N nucleus in the ¹⁵N-labeled complex. Furthermore, the variable-temperature behavior of **2**-(**H**/**D**) is expected in the rapid exchange limit. The large opposing changes in the chemical shifts of the ¹H and ²H signals of **2**-(**H**/**D**) as the temperature was varied are indicative of an equilibrium isotope effect (EIE) wherein D preferentially resides at the amine while H is bound to Mn.¹⁴

The magnitude of the preference for N-D over N-H increased at lower temperatures, consistent with the expected



Figure 4. Qualitative energy diagram for exchange of the proton and hydride sites of 2 via $2 \cdot (\eta^2 \cdot H_2)$ (red) and a depiction of the effect of isotopic substitution.

influence of the zero-point energy (ZPE) differences in the Mn-(H/D) and N-(H/D) bonds (Figure 4). ZPE differences are expected to dominate this equilibrium (Figure S6), in contrast to other systems such as $[M(H)(H_2)]$ studied by Heinekey and others,^{15,16} for which the EIEs may have additional contributions.¹⁴ Those systems can also facilitate rapid H₂ activation, but the nature of the activation is quite different from that in the present system.^{16b}

The temperature dependence of the chemical shifts in 2-(H/**D**) is entirely due to thermodynamics: for the chemical shifts to reflect weighted averages of the different isotopomers, exchange must be fast on the NMR time scale. Assuming the chemical shift of the static hydride in 2-(H/D) to be between -4.5 and -5.5 ppm, we estimate that the EIE for (2-(MnH/ND) \rightleftharpoons 2-(MnD/NH)) is in the range 0.13-0.23 at -20 °C.¹¹ An intramolecular EIE of similar magnitude (K = 0.41 at 56 °C) was observed by Toomey et al.¹⁷ in the amido hydride (η^{5} -C₅(CH₃)₄H)₂Zr(H/D)(N(D/H)^tBu), wherein slow intramolecular H/D exchange facilitated an equilibrium favoring the [Zr(H)][N(D)^tBu] isotopomer.

The rate of the H^+/H^- interconversion in 2 is related to the difference in the frequencies of the two resonances that are being averaged, but the isolated chemical shifts could not be established by "freezing out" the dynamism. In the ¹H NMR spectra of 2 from -25 to -95 °C, the proton-hydride resonance remained coalesced over the entire temperature range (Figure S7A), and similarly, the ²H NMR spectrum of 2-(D/D) remained coalesced down to $-90 \degree C$ (Figure S7B). The ¹H NMR spectra of 2 did show appreciable broadening of the Mn-H/N-H resonance as the temperature was lowered, but concomitant broadening of ligand and solvent resonances suggested that this was due to ion-pair formation and/or an increase in solution viscosity. On the basis of the lowest measured ¹H chemical shift of 2-(H/D) (-4.32 ppm) and the known averaged chemical shift of 2 (2.55 ppm), we estimate a minimum N-H/Mn-H peak separation of 13.7 ppm, corresponding to a reversible heterolytic H₂ cleavage rate greater than 1.5×10^4 s⁻¹ at -95 °C. This minimum rate is consistent with a ΔG^{\ddagger} of less than 6.8 kcal/mol for the overall exchange process. If a similar barrier at room temperature is assumed, H^+/H^- exchange occurs at a rate of at least 10^7 s^{-1} at 25 °C.^{11,18} There are several previous examples of directly observed H^+/H^- exchange,¹⁹ although they occur at substantially lower rates, and others where exchange is implied as part of an overall process.²⁰

The Mn-H and N-H sites are proposed to exchange through an energetically accessible $Mn(\eta^2-H_2)^+$ complex. Exchange between dissolved H_2 and 2 was shown by exchange spectroscopy (EXSY) experiments, which revealed that the Mn-H/N-H resonance was in chemical exchange with free H₂ at an approximate rate of 0.1–10 s⁻¹ at 25 °C (Figure S8). Moreover, addition of H_2 to 1 was only slightly favorable at 1 atm $[\Delta G = -2.1(3) \text{ kcal mol}^{-1}]^{11}$ and removal of the H₂ atmosphere at 20 °C resulted in complete conversion back to red-orange 1 as rapidly as the solution could be degassed. Since no significant HD coupling was observed in 2-(H/D)(expected $J_{\rm HD} \sim 30$ Hz for an η^2 -HD complex),^{15,21} the complex 2-(η^2 -HD) likely lies at least 1 kcal mol⁻¹ above 2-(H/ D). On the basis of this result and the negligible temperature dependence of the ¹H NMR chemical shifts of 2, the intermediate 2-(η^2 -H₂) likely also lies at least 1 kcal mol⁻¹ above 2. Because of the higher energy of $2(\eta^2 - H_2)$ relative to 2, the barrier for heterolytic cleavage of H₂ in this intermediate is correspondingly lower than that for the overall exchange process between the proton and hydride sites in 2 (i.e., $\Delta G^{\ddagger} \leq$ 5.8 kcal mol⁻¹ for H_2 cleavage). Moreover, the temperature dependence of the ¹H NMR signal of 2-(H/D), indicative of the EIE and thus still rapid H^+/H^- exchange, did not show a deviation that would indicate a kinetic isotope effect (KIE). Since a significant primary KIE would be expected for an event involving substantial H-H bond breaking/making, this suggests that the minimum H^+/H^- exchange rate of 1.5 \times 10^4 s⁻¹ at -95 °C may be a considerable underestimate.

Observation of the extremely rapid, reversible heterolytic cleavage of H₂ into a proton and a hydride ion in this bifunctional manganese complex may give insight into synthetic catalysts and enzymes that heterolytically cleave H₂. Energy matching between the heterolytic cleavage product and the $Mn(\eta^2 - H_2)^+$ complex was obtained, such that exchange between the Mn-H and N-H sites was facile. The rate of the overall exchange has been estimated to be $>10^7$ s⁻¹ at 25 °C, which is orders of magnitude higher than the rates of catalysis for H₂ oxidation or production in [FeFe] hydrogenase⁵ and reported molecular catalysts that mimic the function of this enzyme.²² The facility of H₂ activation shown here suggests that other suitably energy-matched systems may be able to perform facile heterolysis of nonpolar substrates, an as-yet underutilized strategy in the activation of, for example, alkane C-H bonds.

ASSOCIATED CONTENT

S Supporting Information

Experimental procedures, syntheses, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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