Reversible Heterolytic Cleavage of the H–H Bond by Molybdenum Complexes: Controlling the Dynamics of Exchange Between Proton and Hydride

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Supporting Information

ABSTRACT: Controlling the heterolytic cleavage of the H–H bond of dihydrogen is critically important in catalytic hydrogenations and in the catalytic oxidation of H2. We show how the rate of reversible heterolytic cleavage of H2 can be controlled, spanning 4 orders of magnitude at 25 °C, from 2.1 × 10^7 s⁻¹ to ≥10¹⁰ s⁻¹. Bifunctional Mo complexes, [CpMo(CO)({κ²,P,N}_2)]⁺ (P,N_2 = 1,5-diaza-3,7-diphosphacyclooctane diphosphine ligand with alkyl/aryl groups on N and P), have been developed for heterolytic cleavage of H2 into a proton and a hydride, akin to frustrated Lewis pairs. The H–H bond cleavage is enabled by the basic amine in the second coordination sphere. The products of heterolytic cleavage of H2 Mo hydride complexes bearing protonated amines, [CpMo(H)(CO)(P,N_2H)]⁺, were characterized by spectroscopic studies and by X-ray crystallography. Variable-temperature 1H, 15N, and 2-D 1H ROESY NMR spectra indicated rapid exchange of the proton and hydride. The exchange rates are in the order [CpMo(H)(CO)(P,N_2H)]⁺ > [CpMo(H)(CO)(P,N_2H)]⁰ > [CpMo(H)(CO)(P,N_2H)]⁻ > [CpMo(H)(CO)(P,N_2H)]⁻. The pKₐ values determined in acetonitrile range from 9.3 to 17.7 and show a linear correlation with the logarithm of the exchange rates. This correlation likely results from the exchange process involving key intermediates that differ by an intramolecular proton transfer. Specifically, the proton-hydride exchange appears to occur by formation of a molybdenum dihydride or dihydrogen complex, resulting from proton transfer from the pendant amine to the metal hydride. The exchange dynamics are controlled by the relative acidity of the [CpMo(H)(CO)(P,N_2H)]⁺ and [CpMo(H)(CO)(P,N_2H)]⁻ isomers, providing a design principle for controlling heterolytic cleavage of H2.

INTRODUCTION

The H–H bond is the simplest chemical bond, yet it offers diverse reactivity.¹⁻⁶ Cleavage of the H–H bond is a fundamentally important reaction that can occur by homolytic or heterolytic pathways. Heterolytic cleavage of the H–H bond into a proton and hydride (Scheme 1) is a critical process in the catalytic hydrogenation of ketones,⁵⁻⁷ the oxidation of hydrogen by hydrogenases in nature¹⁰ and by synthetic molecular catalysts.¹⁸⁻¹⁴ Interest in using H2 as a clean fuel produced through sustainable solar and wind energy has propelled research on finding facile ways to cleave the H–H bond. Understanding the fundamental thermodynamics and kinetics of heterolytic H–H bond cleavage and controlling the transfer of the proton and hydride are critically important for the design of new catalysts.

Frustrated Lewis pairs (FLPs) based on main group elements have shown remarkable reactivity in heterolytic cleavage of the H–H bond, leading to the development of new classes of hydrogenation catalysts.¹⁵⁻²⁰ Steric hindrance or ring strain prevent the Lewis acid and base centers from forming an adduct. The “unquenched” reactivity of FLPs creates a polarized environment that facilitates heterolytic cleavage of the H–H bond. Some “not-so-frustrated” Lewis acid/base adducts reversibly expose the Lewis acidic and basic centers in an equilibrium, leading to reactivity similar to that of traditional FLPs.²¹⁻²⁶ Wiss and co-workers called attention²⁷,²⁸ to the relationship between main group FLPs and reactions in which a transition metal functions as a Lewis acid or base.²⁷⁻³⁶ Transition-metal containing FLPs can be considered in the broader context of metal–ligand bifunctional catalysis³⁷ and metal–ligand cooperation³⁸⁻⁴¹ in catalysis. A recent perspective article reviews the heterolytic cleavage of H2 in the framework of metal-containing FLPs.⁴²

Heterolytic cleavage of the H–H bond in many bifunctional complexes is enabled by an amine as a proton acceptor in the second coordination sphere, and the metal as the hydride acceptor, mimicking the function of hydrogenase.⁵,⁹ An important application of the heterolytic cleavage of H2 is ionic hydrogenations and in the catalytic oxidation of H2. We show how the rate of reversible heterolytic cleavage of H2 can be controlled, spanning 4 orders of magnitude at 25 °C, from 2.1 × 10^7 s⁻¹ to ≥10¹⁰ s⁻¹. Bifunctional Mo complexes, [CpMo(CO)({κ²,P,N}_2)]⁺ (P,N_2 = 1,5-diaza-3,7-diphosphacyclooctane diphosphine ligand with alkyl/aryl groups on N and P), have been developed for heterolytic cleavage of H2 into a proton and a hydride, akin to frustrated Lewis pairs. The H–H bond cleavage is enabled by the basic amine in the second coordination sphere. The products of heterolytic cleavage of H2 Mo hydride complexes bearing protonated amines, [CpMo(H)(CO)(P,N_2H)]⁺, were characterized by spectroscopic studies and by X-ray crystallography. Variable-temperature 1H, 15N, and 2-D 1H ROESY NMR spectra indicated rapid exchange of the proton and hydride. The exchange rates are in the order [CpMo(H)(CO)(P,N_2H)]⁺ > [CpMo(H)(CO)(P,N_2H)]⁰ > [CpMo(H)(CO)(P,N_2H)]⁻ > [CpMo(H)(CO)(P,N_2H)]⁻. The pKₐ values determined in acetonitrile range from 9.3 to 17.7 and show a linear correlation with the logarithm of the exchange rates. This correlation likely results from the exchange process involving key intermediates that differ by an intramolecular proton transfer. Specifically, the proton-hydride exchange appears to occur by formation of a molybdenum dihydride or dihydrogen complex, resulting from proton transfer from the pendant amine to the metal hydride. The exchange dynamics are controlled by the relative acidity of the [CpMo(H)(CO)(P,N_2H)]⁺ and [CpMo(H)(CO)(P,N_2H)]⁻ isomers, providing a design principle for controlling heterolytic cleavage of H2.

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Scheme 1. Heterolytic H–H Bond Cleavage

H–H \[ \xrightarrow{M} \] H⁺ + H⁻
The proton and hydride are subsequently delivered to the unsaturated substrate, without requiring coordination of the substrate to the metal.37 Tuning the ability of the proton3 and hydride4 to be transferred to a substrate has a strong impact on the kinetics and thermodynamics and consequently on the catalytic activity for ionic hydrogenations. Thus, the ability to understand and control the factors influencing rates of heterolytic cleavage of H2 is important.

Heterolytic activation of the H–H bond by Mo complexes is rare;48,49 Berke and co-workers reported heterolytic cleavage of H2 across a Mo=O bond in [(R3PCH2CH2)2N]Mo(NO)-(CO)46. The product, [(R3PCH2CH2)2NH]Mo(H)(NO)-(CO), was identified by NMR spectroscopy, but it is unstable in the absence of H2. Molybdenum complexes reported by Long, Chang, and co-workers are electrocatalysts for the evolution of H2 in aqueous solution.50 The proton and hydride are subsequently delivered to the substrate, without requiring coordination of the hydride to a substrate has a strong impact on the kinetics and thermodynamics and consequently on the catalytic activity for ionic hydrogenations.

In this paper, we report the facile heterolytic cleavage of H2 by cationic Mo complexes, affording Mo hydride complexes bearing a protonated amine, [CpMo(H)(CO)(PR2NHR)]+ (Scheme 2).68 These results suggest that the amine is strongly bound to the electrophilic Mo center because of the wide P–Mo–P angle of the flexible PNP ligand.

The amine-bound proton and the metal hydride undergo rapid exchange,63,64,65,66,69,70 demonstrating reversible cleavage and heterocoupling of the H–H bond. The pK value quantitatively reveal that tuning the acidity of the complexes controls the rates of reversible heterolytic cleavage by about 4 orders of magnitude. The more acidic [CpMo(H)(CO)(PR2NR2)]+ complexes show faster exchange rates of the proton and hydride, demonstrating the ability to control the reaction by changing the substituents on the phosphine and amine.

### Scheme 2. Heterolytic Cleavage of H2 by a FLP and Mo Complexes

<table>
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Inspired by the structure–function relationships established in main group and transition-metal-based FLPs, we anticipated that structural modification of the ligand by introducing ring strain to destabilize the Mo–N coordination might reversibly expose a vacant coordination site for reaction with H2, allowing the Lewis acidic Mo center and the basic amine to provide cooperative heterolytic H–H bond cleavage.

In this paper, we report the facile heterolytic cleavage of H2 by cationic Mo complexes, affording Mo hydride complexes bearing a protonated amine, [CpMo(H)(CO)(PR2NR2)]+ (Scheme 2).

### Results

#### Synthesis and Characterization of CpMoH(CO)(P2N2) Complexes. CpMoH(CO)(PPh2)2 (PhPhMoH, R = Ph; PhPhMoH, R = Ph) with Ph groups on the phosphines were synthesized from CpMoH(CO)3 and the diphosphine ligand PPh2NR2 in toluene at 80 °C (Scheme 3), similar to the route used in the synthesis of CpMoH(CO)(PPh2NR2) complexes (R = Et, Ph).67 The Mo hydride complex PhPhMoH was isolated in 73% yield, and its structure was confirmed by single-crystal X-ray diffraction (Figure 1, Table S14). A doublet of doublets at −6.83 ppm (JH = 57 Hz for cis; JH = 18 Hz for trans) was observed in the 1H NMR spectrum as the hydride resonance of PhPhMoH in CD2Cl2, as expected for hydride ligands coupled to both cis and trans phosphines.

For the analogous CpMo(CO)(PPh2NR2) complex, a similar route to PhPhMoH was devised. The Mo chloride complexes, CpMoCl(CO)(PPh2NR2) (BuMoCl, R = Bu; BuMoCl, R = Bu) complexes bearing Ph groups on the phosphines, attempted synthesis by the reaction of CpMoH(CO)3 and PPh2NR2 in either hexane or benzene at 80 °C resulted in a mixture of BuMoCl and other products that have not been identified. An alternative synthetic route to BuMoCl was devised. The Mo chloride complexes, CpMoCl(CO)(PPh2NR2) (BuMoCl, R = Bu; BuMoCl, R = Bu) complexes bearing Ph groups on the phosphines, attempted synthesis by the reaction of CpMoH(CO)3 and PPh2NR2 at 110 °C in toluene, followed by treatment with Me3NO in CH2Cl2 leading to oxidative elimination of one CO ligand. The corresponding Mo hydrides BuMoCl were prepared from the reaction of BuMoCl with...
Mo hydrides vary over the narrow range from 74.103(15)° to 75.219(17)°. In the 31P{1H} NMR spectra, the chemical shifts of the 31P NMR resonances range from 2.0 to 6.9 ppm, comparable to other 3-PNP or 3-P2N metal complexes featuring methyls of tert-butyl groups, and hydrogen atoms are omitted for clarity, except for the ipso-C of the phenyl group and Mo−H.

LiBHET₃ in THF (Scheme 3). The X-ray crystallographic structures of Ph₃MoH, Bu₃MoCl, Bu₃MoCl, Bu₃MoH, and Bu₃PbMoH all show four-legged piano-stool geometries and cis geometries of the two phosphines (Figure 1; see SI for the structure of Bu₃PbMoCl). The P−Mo−P bond angles of these Mo hydrides vary over the narrow range from 74.103(15)° to 75.219(17)°.

Synthesis and Characterization of [CpMo(CO)(κ²-P₂N₂)][+], Cationic Mo Diphosphine Complexes Bearing a Bound Amine. The cationic “tuck-in” Mo complexes [CpMo(CO)(κ²-P₂N₂)][+][BAR₄]− ([Bu₃PbMo][+], R’ = Bn; [Bu₃PPhMo][+], R’ = Ph; [Bu₃PPhMo][+], R’ = Bu) were prepared by chloride abstraction from [Bu₃MoCl] using NaBAR₄ (ArF = 3,5-bis(trifluoromethyl)phenyl) in fluorobenzene and were fully characterized (Scheme 4). In the 31P{1H} NMR spectra, the chemical shifts of the 31P NMR resonances range from −2.0 to 6.9 ppm, comparable to other κ²-PNP or κ²-P₂N₂ metal complexes featuring four-membered phosphacycles. Even though the structures of [Bu₃Mo][+] and [CpMo(CO)(κ²-P₂N₂)][+] (Figure 2, Table S1) all show the κ² coordination mode, with the amine bound, the P−Mo−P bond angles of [Bu₃Mo][+] (85.636(17)°) to 87.75(2)° are much smaller than the wide P−Mo−P angles found in [CpMo(CO)(κ²-P₂N₂)][+] (123.220(16)°) and [CpMo(CO)(κ²-P₂N₂)][+][BAR₄]− (122.20(2)°). The Mo−N bond lengths in [Bu₃Mo][+] (2.370(3) Å), [Bu₃PbMo][+] (2.405(2) Å), and [Bu₃PPhMo][+] (2.4583(16) Å) are significantly longer than the values of 2.3083(13) Å in the [CpMo(CO)(κ²-P₂N₂)][+] and [CpMo(CO)(κ²-P₂N₂)][+][BAR₄]−, suggesting the Mo−N bond strength of [Bu₃Mo][+] is weaker.

The complex [CpMo(CO)(κ²-P₂N₂)][+] ([Ph₃PbMo][+]*, R’ = Bn; [Ph₃PPhMo][+], R’ = Ph) was generated in situ by hydride abstraction from Ph₃MoH or Ph₃PbMoH with [Ph₃C][BAR₄]− in fluorobenzene (Scheme 5). The X-ray crystallographic structure of [Ph₃Mo][+] [BAR₄]− unambiguously confirmed the connectivity and the κ²-coordination mode, despite some disorder of heavy atoms (see Supporting Information). Furthermore, we reported the slow reaction (3 h) of [CpMo(CO)(κ²-P₂N₂)][+] [BAR₄]− ([Ph₃Mo][+] [BAR₄]−, left) and [CpMo(CO)(κ²-P₂N₂)][+][BAR₄]− ([Bu₃PbMo][+] [BAR₄]−, right) with 30% thermal ellipsoids. BAR₄− anions, methyls of tert-butyl groups, and hydrogen atoms are omitted for clarity.
order kinetics of its solvolysis in acetonitrile ($\Delta H^\ddagger = 21.6 \pm 2.8$ kcal/mol, $\Delta S^\ddagger = -0.3 \pm 9.8$ cal/(mol·K)). In contrast, dissociation of the amine in [Ph$_3$Mo]$^+$ and addition of an acetonitrile ligand occurred rapidly at 0 °C, as indicated by a color change from violet to yellow, and was complete within seconds. The high reactivity of electrophilic Mo complexes toward acetonitrile, as found for [CpMo(CO)$_2$(P)$_3$(Me)[$^+$B(C$_6$F$_5$)$_4$] complex toward acetonitrile, as found for [CpMo(CO)$_2$(P)$_3$(Me)[$^+$B(C$_6$F$_5$)$_4$] immediately at room temperature, as found for [CpMo(CO)$_2$(P)$_3$(Me)[$^+$B(C$_6$F$_5$)$_4$] immediately at 0 °C, indicating the displacement of the acetonitrile ligand by H$_2$ is unfavorable without elimination of H$_2$. In MeCN, it loses H$_2$ very slowly, reaching completion after 24 h at room temperature. Deprotection of [Ph$_3$MoH(NH)$_2$] by Et$_3$N ($pK_a = 18.87$ for H-NEt$_3$ in MeCN) generates the corresponding neutral Mo hydride complexes Ph$_3$MoH.

In CD$_3$CN, [Ph$_3$Mo]$^+$ complexes rapidly bind CD$_3$CN and form [CpMo(CO)($^3$PR$_2$2)(CD$_3$CN)]$^+$, [Ph$_3$Mo(CD$_3$CN)]$^+$, as observed by $^{31}$P NMR spectra. Addition of H$_2$ to [Ph$_3$Mo(CD$_3$CN)]$^+$ was not observed in CD$_3$CN solution, indicating the displacement of the acetonitrile ligand by H$_2$ is unfavorable thermodynamically and/or kinetically. Thus, we were not able to measure the hydricity of Ph$_3$MoH or the kinetic barrier for H$_2$ addition to [Ph$_3$Mo(CD$_3$CN)]$^+$ in CD$_3$CN. In contrast, [Ph$_3$MoH(NH)$_2$] is stable in THF without elimination of H$_2$. In MeCN, it loses H$_2$ slowly, reaching completion after 24 h at room temperature, [Ph$_3$MoH(NH)$_2$] in MeCN. Addition of H$_2$ to [Ph$_3$Mo(CD$_3$CN)]$^+$ was not observed in CD$_3$CN solution, indicating the displacement of the acetonitrile ligand by H$_2$ is unfavorable thermodynamically, slow, or kinetically. In contrast, [Ph$_3$MoH(NH)$_2$] is stable in THF or MeCN solvent without elimination of H$_2$. In MeCN, it loses H$_2$ very slowly, reaching completion after 24 h at room temperature. Deprotection of [Ph$_3$MoH(NH)$_2$] by Et$_3$N ($pK_a = 18.87$ for H-NEt$_3$ in MeCN) generates the corresponding neutral Mo hydride complexes Ph$_3$MoH.

Orange crystals of both [Ph$_3$MoH(NH)$_2$][BAr$_4^-$] and [Ph$_3$MoH(NH)$_2$][BAr$_4^-$] were grown by slow diffusion of pentane into a fluorobenzene solution under H$_2$ (1 atm). The X-ray crystallographic analysis reveals structures containing both Mo–H and N–H bonds, resulting from heterolytic cleavage of H$_2$. Surprisingly, [Ph$_3$MoH(NH)$_2$] and [Ph$_3$MoH(NH)$_2$] adopt different conformational geometries (Figure 3). [Ph$_3$MoH(NH)$_2$] crystallized as the anti, enol-isomer. The proton and hydride are arranged on different sides of the P–Mo–P plane (H···H distance ~4.15 Å) instead of being positioned close to each other on the same side. In contrast, the crystal structure of [Ph$_3$MoH(NH)$_2$] indicated the syn, endo-isomer, with the proton and hydride positioned toward each other (Figure 3, middle). The Mo–H bond length determined by X-ray diffraction is 1.628(9) Å, though the precise location of hydride is subject to the uncertainties associated with X-ray crystallography. Setting the N–H distance to 1.000 Å gives an estimated H–H distance of 2.456 Å. This distance is much longer than the short H–H distance of 1.489(10) Å found for dihydrogen bonding in the single crystal neutron diffraction structure of [CP$^{CP4F4}$Fe(H)(P$_{Bu_2}^2$N$_{Bu_2}$H)]$^+$[BAr$_4^-$] (Figure 3, top). In this structure, the N–H bond is positioned in close proximity to the iron hydride in the three-legged piano stool coordination geometry. Ph$_3$MoH(NH)$_2$ has one additional CO ligand, adopting a four-legged piano stool coordination geometry. The rigid P$_2$N$_2$ ligand could only form the cis configuration instead of trans configuration. As a result, the hydride from heterolytic cleavage of the H–H bond is located trans to one phosphine, instead of cis to two phosphines in [1].
phosphine, affording \([\text{Bu}^3\text{MoH}^+\text{(NH)}]^+\) (Scheme 5). All three complexes \([\text{Bu}^3\text{MoH}^+\text{(NH)}]^+\) are stable in MeCN solution, in the solid state under an \(N_2\) atmosphere or under vacuum. Crystals of \([\text{Bu}^3\text{MoH}^+\text{(NH)}]^+\) and \([\text{Bu}^3\text{P}^3\text{MoH}^+\text{(NH)}]^+\) were grown by slow diffusion of pentane into a fluorobenzene solution, and their structures were characterized by X-ray crystallography as syn, endo-isomers (Figures 3 and S3).

We propose that \([\text{R}^R\text{MoH}^+\text{(NH)}]^+\) is formed through intramolecular deprotonation of an unobserved Mo dihydride or dihydrogen intermediate (Scheme 6).\(^{76}\) Attempts to observe intramolecular deprotonation of an unobserved Mo dihydride \([\text{MoH}^-\text{Two}^2\text{H}]^+\) were unsuccessful, as rapid heterolytic bond cleavage was achieved in variable-temperature \(1\text{H}, 31\text{P}, 15\text{N}, \text{and 2-D NMR spectra of \([\text{MoH}^-\text{Two}^2\text{H}]^+\) reveal rapid exchange of the proton and hydride at 20 °C, indicating that the H–H bond is rapidly, reversibly formed and heterolytically cleaved.

The \(1\text{H} \) NMR spectrum of \([\text{PhBu}^3\text{MoH}^+\text{(NH)}]^+\) in THF-\(d_8\) at 20 °C shows a broad singlet integrating to two protons at \(-0.15 \text{ ppm (Figure 4). No separate proton or hydride resonance}\)

![Figure 4. Variable-temperature \(1\text{H} \) NMR spectra of \([\text{PhBu}^3\text{MoH}^+\text{(NH)}]^+\) in THF-\(d_8\).](image)

was found in the typical chemical shift regions of Mo\((\eta^2\text{-H}_2)^+\) (−2 to −5 ppm), Mo\((\text{H})_2^+\) (−3 to −6 ppm), a structure containing a Mo–H bond (−5 to −9 ppm) or a N–H bond of the protonated P\(_2\)N\(_2\) ligand (14 to 7 ppm). We assign the resonance at −0.15 ppm in \(1\text{H} \) NMR spectrum to the rapidly exchanging N–H and Mo–H resonances.

Since only one of the two amines is protonated, the assignment of the structure with dynamic proton-hydride exchanging character was further confirmed by \(15\text{N} \) NMR and \(1\text{H}–15\text{N} \) HSQC spectra. In the \(15\text{N} \) NMR spectrum of \(15\text{N}\)-labeled \([\text{PhBu}^3\text{MoH}^+\text{(NH)}]^+\), the resonance of the protonated amine exhibits a triplet of triplets at −305 ppm (\(J_{\text{HN}} = 35 \text{ Hz}, J_{\text{NP}} = 5.7 \text{ Hz}\)), indicating coupling between this \(15\text{N} \) nucleus and two equivalent protons. The magnitude of \(J_{\text{HN}}\) is close to the average value of a nonexchanging N–H bond in a protonated amine (−70 Hz) and negligible \(15\text{N} \) coupling (−0 Hz) to the hydride, showing the rapid proton–hydride exchanging dynamics.

The nitrogen of the other pendant amine showed a triplet at −340 ppm with \(J_{\text{NP}} = 11.5 \text{ Hz}\) and no direct N–H coupling. No “pinched” exo-isomer featuring a bridging proton between two nitrogens of the pendant amine (N–H–N) was observed.\(^{78}\)

The solution structure of \([\text{PhBu}^3\text{MoH}^+\text{(NH)}]^+\) at 20 °C shows dynamic intramolecular proton-hydride exchange of the Mo–H and N–H resonances, in contrast with its anti, endo structure in
solid state that shows no interaction of the amine-bound proton and Mo hydride.

When a THF-d$_6$ solution of [Ph$_3$BuMoH(NH)]$^+$ was cooled to −20 °C, the broad singlet of the exchanging proton and hydride coalesced into the baseline of the $^1$H NMR spectrum, indicating a decrease in the rate of dynamic exchange. Decoalescence was reached at −40 °C, and two new broad singlets were observed, assigned to resonances of an amine-bound proton and a Mo hydride. At −80 °C, these two resonances appear as a broad singlet at 6.54 ppm and a doublet of doublets at −6.70 ppm ($J_{HH} = 54$ Hz for cis; $J_{HP} = 21$ Hz for trans). In the $^{13}$N NMR spectrum, the protonated nitrogen appeared as a broad doublet at −309 ppm with $J_{HN} = 71$ Hz in $^{15}$N-labeled [Ph$_3$BuMoH(NH)]$^+$. A $^1$H−$^{15}$N HSQC spectrum of $^{15}$N-labeled [Ph$_3$BuMoH(NH)]$^+$ in THF-d$_6$ at −60 °C exhibits a cross peak between the nitrogen resonance at −309 ppm and the proton resonance at 6.49 ppm, but not with the hydride resonance (Figure S61). $^1$H−H NOESY and ROESY NMR spectra both exhibit cross peaks between proton and hydride resonances at −80 °C, suggesting the amine-bound proton and metal hydride still exchange at −80 °C, though with a relatively slow rate (Figures S57 and S58).

The observed $T_1$ relaxation time for the individual Mo−H and N−H resonances of [Ph$_3$BuMoH(NH)]$^+$ are nearly the same (400 ms for N−H and 360 ms for Mo−H at −30 °C), both decreasing from 1.5 s (at −80 °C) to a minimum of 360 ms at −30 °C in THF-d$_6$ (Figure S55). For the averaging Mo−H−H−N resonance at −0.15 ppm in fluorobenzene, the minimum $T_1$ value is 378 ms at −10 °C, which is much shorter than the typical $T_1$ value of Mo hydride complexes (>1 s). Thus, the observed short $T_1$ relaxation time indicates the presence of a Mo−H−H−N interaction in [Ph$_3$BuMoH(NH)]$^+$ and reveals that the rate of proton-hydride exchange is a function of temperature. Morris and co-workers also observed the resonance of an interacting proton-hydride had a shorter $T_1$ relaxation time than that of the metal hydride because of “$T_1$ averaging.”

The spectroscopic data suggest rapid exchange of the amine-bound proton and the Mo hydride in [Ph$_3$BuMoH(NH)]$^+$ above 20 °C. The dynamic NMR spectra allowed measurement of the kinetics of exchange in different solvents. The pseudo-first-order rates of exchange of the proton and hydride at 25 °C were determined by simulation of the variable-temperature NMR spectra as $k = 3.9 \times 10^9$ s$^{-1}$ (in THF) and $1.7 \times 10^9$ s$^{-1}$ (in CH$_2$Cl$_2$) (Figure 5). Activation parameters were determined from an Eyring analysis, in all cases over at least a 100$^0$ range, and are given in Table 1. The rate of exchanging proton and hydride is five times faster in CH$_2$Cl$_2$ than in THF, which could result from the changes in the relative acidities and/or variations in hydrogen bonding in the different solvents.

The complex [Ph$_3$BuMoH(NH)]$^+$, with phenyl groups on the amines, shows strikingly different $^1$H NMR spectroscopic characteristics. At 20 °C, a 1:2:1 triplet integrating to two protons was observed at −0.51 ppm in CD$_2$Cl$_2$ (−0.81 ppm in fluorobenzene) with $J_{HH} = 21$ Hz, which is assigned as the rapidly exchanging proton and hydride (Figure 6, left). In the $^{15}$N-labeled complex, this resonance appears as a quartet in the $^1$H NMR spectrum and as a doublet in the $^{13}$H($^{31}$P) NMR spectrum. In the $^{13}$N NMR spectrum, the $^{15}$N nucleus coupled to the Mo−H/N−H resonance exhibits a triplet of triplets at −302 ppm ($J_{HN} = 23$ Hz, $J_{NP} = 7.5$ Hz) at 20 °C. We propose that the averaging Mo−H/N−H resonance couples with $^{15}$N and that the $J_{HN}$ is coincidently the same as the $J_{HP}$ value of 21 Hz. Rapid proton-hydride exchange of the Mo−H and N−H resonances was also identified by the cross peak between the nitrogen resonance and the hydride resonance at −0.81 ppm in the $^1$H−$^{15}$N HSQC spectrum at 20 °C (Figure S62).

Cooling a CD$_2$Cl$_2$ solution of [Ph$_3$BuMoH(NH)]$^+$ to −90 °C led to broadening of the exchanging proton and hydride resonances, without reaching decoalescence in the $^1$H NMR spectrum. The triplet observed at 20 °C collapses into a broad singlet at 0.38 ppm at −90 °C, with no separate proton and hydride resonances observed in the typical regions, suggesting that exchange of proton and hydride remains extremely fast, even at −90 °C. The Mo−H/N−H resonance shows temperature-dependent behavior, shifting downfield from −0.51 ppm at 20 °C to 0.38 ppm at −90 °C.

Addition of HD gas to a solution of [Ph$_3$BuMoH(NH)]$^+$ in fluorobenzene, or adding [D(OEt)$_2$]$_2$[BC(CF$_3$)$_4$] to Ph$_3$BuMoH in CH$_2$Cl$_2$ at 20 °C, gave an equilibrium [Ph$_3$BuMoH(ND)]$^+$⇌[Ph$_3$BuMoD(NH)]$^+$. Variable-temperature $^1$H and $^2$H NMR spectroscopic studies reveal an equilibrium isotope effect (EIE) 10.69. At 20 °C, a triplet at −3.73 ppm (1H, $J_{HD} = 29$ Hz) in the $^2$H NMR spectrum appears near the typical chemical shift of Mo hydride resonances; a resonance was observed at 3.09 ppm in the $^2$H NMR spectrum. The average of the $^1$H and $^2$H chemical shifts (−0.31 ppm) is close to the value of the averaging Mo−H/N−H resonance of [Ph$_3$BuMoH(NH)]$^+$ (−0.51 ppm). Upon cooling a solution of the HD adduct, the chemical shift exhibiting predominantly metal hydride character gradually shifts upfield from −3.73 ppm (20 °C) to −5.72 ppm (−90 °C) in the $^2$H NMR spectrum, while the deuterium resonance shifts in the opposite direction, downfield from 3.09 ppm (40 °C) to 5.97 ppm (−70 °C) in the $^2$H NMR spectrum (Figure S67). Thus, the disparity $^1$H and $^2$H chemical shifts of [Ph$_3$BuMoH(ND)]$^+$⇌[Ph$_3$BuMoD(NH)]$^+$ result from an EIE that favors the Mo−H/N−D isotope energetically over the Mo−D/N−H isotope, as a result of the larger zero-point energy differences of the N−H/N−D bonds compared to the Mo−D/Mo−H bonds. At lower temperature, the relative population of [Ph$_3$BuMoH(ND)]$^+$ increases and that of [Ph$_3$BuMoD(NH)]$^+$ decreases, indicating that [Ph$_3$BuMoD(NH)]$^+$ is increasingly thermodynamically favored at lower temperatures. An EIE of 0.22−0.29 at −20 °C is estimated.69

Determination of the rate of reversible heterolytic cleavage of the H−H bond in [Ph$_3$BuMoH(NH)]$^+$ requires knowledge of the peak separation of the two resonances that are being averaged. Since the “frozen-out” Mo−H and N−H resonances in
both exhibit cross peaks at $-70^\circ C$. The minimum peak separation of the Mo−H and N−H resonances is 12.2 ppm estimated for the “frozen out” structure of $[\text{PPh}_2\text{MoH}(\text{NH})]$+, which corresponds to a lower limit of the reversible heterolytic H−H bond cleavage rate as $1.4 \times 10^{-4}$ s$^{-1}$ at our lowest temperature, $-90^\circ C$. The average chemical shift of $[\text{PPh}_2\text{MoH}(\text{ND})]$+ ($-5.72$ ppm at $-90^\circ C$). A minimum peak separation of the Mo−H and N−H resonances of 12.2 ppm is estimated for the “frozen out” structure of $[\text{PPh}_2\text{MoH}(\text{NH})]$+.

The rate of exchange between the proton and hydride at $25^\circ C$ was determined from simulation of the dynamic $^1H$ NMR spectra as $k = 6.9 \times 10^6$ s$^{-1}$ (THF) and $1.4 \times 10^6$ s$^{-1}$ (CH$_2$Cl$_2$).

Changing the substituent on the amine from benzyl to phenyl in $[\text{BuPhMoH}(\text{NH})]^+$ leads to more rapid exchange dynamics, as found in $[\text{Ph}_3\text{P}\text{MoH}(\text{NH})]^+$ analogues. The Mo−H/N−H resonance of $[\text{BuPhMoH}(\text{NH})]^+$ exhibits a 1:2:1 triplet at $-1.49$ ppm with $\Delta J_{\text{HH}} = 24$ Hz in CD$_2$Cl$_2$ at $20^\circ C$ (Figure 6, right). The Mo−H/N−H resonance is broadened upon cooling the solution and merged into the baseline at $-80^\circ C$ without showing separate proton and hydride resonances, indicating decaolalence was reached. Variable-temperature $^1H$ and $^2H$ NMR spectra of the HD adduct $[\text{BuPhMoH}(\text{ND})]^+$ show dynamic exchange of H and D between the amine and Mo and an EIE (see Supporting Information for details). Using the average chemical shift of Mo−H/N−H resonance ($-0.49$ ppm at $-60^\circ C$) and the lowest measured $^1H$ chemical shift of $[\text{BuPhMoH}(\text{ND})]^+$ ($-5.03$ ppm at $-60^\circ C$), a minimum peak separation of the Mo−H and N−H resonances was estimated at 9.08 ppm for $[\text{BuPhMoH}(\text{NH})]^+$. Thus, the lower limit of exchange rate of proton and hydride in CH$_2$Cl$_2$ is estimated as $1.0 \times 10^6$ s$^{-1}$ at $-60^\circ C$ ($\Delta G^\ddagger < 8.4$ kcal mol$^{-1}$) and $4.1 \times 10^6$ s$^{-1}$ at $25^\circ C$, if $\Delta G^\ddagger$ is the same at both temperatures. Thus, the exchange rate of proton and hydride in

<table>
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<th>solvent</th>
<th>$\Delta H^\ddagger$ (kcal mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (cal K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G^\ddagger$ (298 K, kcal mol$^{-1}$)</th>
<th>$k$ (298 K, s$^{-1}$)</th>
<th>$pK_a$ in CH$_2$CN</th>
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<td>$[\text{PPh}_2\text{MoH}(\text{NH})]^+$</td>
<td>THF-$d_8$</td>
<td>13.2 ± 0.7</td>
<td>11.1 ± 2.8</td>
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<td>9.1 ± 0.7</td>
<td>0.5 ± 3.1</td>
<td>8.9 ± 1.2</td>
<td>1.7 × 10$^6$</td>
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<tr>
<td>$[\text{Ph}_3\text{P}\text{MoH}(\text{NH})]^+$</td>
<td>CD$_2$Cl$_2$</td>
<td>7.1$^b$</td>
<td>4.0 × 10$^7$</td>
<td>9.3 ± 0.1</td>
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<tr>
<td>$[\text{BuPhMoH}(\text{NH})]^+$</td>
<td>THF-$d_8$</td>
<td>12.0 ± 0.6</td>
<td>3.8 ± 2.3</td>
<td>10.9 ± 0.9</td>
<td>6.9 × 10$^4$</td>
</tr>
<tr>
<td></td>
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<td>10.9 ± 0.7</td>
<td>1.5 ± 2.8</td>
<td>10.4 ± 1.1</td>
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<td>$[\text{BuPhMoH}(\text{NH})]^+$</td>
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<td>8.4$^b$</td>
<td>4.1 × 10$^6$</td>
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<tr>
<td>$[\text{BuPhMoH}(\text{NH})]^+$</td>
<td>THF-$d_8$</td>
<td>9.1 ± 1.0</td>
<td>$-12.9$ ± 3.8</td>
<td>12.9 ± 1.5</td>
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$^a$Reported uncertainties are twice the standard deviation. $^b$Estimated value; see text.

**Figure 6.** Variable-temperature $^1H$ NMR spectra of $[\text{CpMo}(\text{H})(\text{CO})-\text{(PPh}_2\text{NPh}_2\text{H})]^+$ (left) and $[\text{CpMo}(\text{H})(\text{CO})-\text{(PPh}_2\text{NPh}_2\text{H})]^+$ (right) in CD$_2$Cl$_2$.

**Figure 7.** Variable-temperature $^1H$ NMR spectra of $[\text{CpMo}(\text{H})(\text{CO})-\text{(PPh}_2\text{NPh}_2\text{H})]^+$ in THF-$d_8$. The rate of exchange between the proton and hydride at $25^\circ C$ was determined from simulation of the dynamic $^1H$ NMR spectra as $k = 6.9 \times 10^6$ s$^{-1}$ (THF) and $1.4 \times 10^6$ s$^{-1}$ (CH$_2$Cl$_2$). Changing the substituent on the amine from benzyl to phenyl in $[\text{BuPhMoH}(\text{NH})]^+$ leads to more rapid exchange dynamics, as found in $[\text{Ph}_3\text{P}\text{MoH}(\text{NH})]^+$ analogues. The Mo−H/N−H resonance of $[\text{BuPhMoH}(\text{NH})]^+$ exhibits a 1:2:1 triplet at $-1.49$ ppm with $\Delta J_{\text{HH}} = 24$ Hz in CD$_2$Cl$_2$ at $20^\circ C$ (Figure 6, right). The Mo−H/N−H resonance is broadened upon cooling the solution and merged into the baseline at $-80^\circ C$ without showing separate proton and hydride resonances, indicating decaolalence was reached. Variable-temperature $^1H$ and $^2H$ NMR spectra of the HD adduct $[\text{BuPhMoH}(\text{ND})]^+$ show dynamic exchange of H and D between the amine and Mo and an EIE (see Supporting Information for details). Using the average chemical shift of Mo−H/N−H resonance ($-0.49$ ppm at $-60^\circ C$) and the lowest measured $^1H$ chemical shift of $[\text{BuPhMoH}(\text{ND})]^+$ ($-5.03$ ppm at $-60^\circ C$), a minimum peak separation of the Mo−H and N−H resonances was estimated at 9.08 ppm for $[\text{BuPhMoH}(\text{NH})]^+$. Thus, the lower limit of exchange rate of proton and hydride in CH$_2$Cl$_2$ is estimated as $1.0 \times 10^6$ s$^{-1}$ at $-60^\circ C$ ($\Delta G^\ddagger < 8.4$ kcal mol$^{-1}$) and $4.1 \times 10^6$ s$^{-1}$ at $25^\circ C$, if $\Delta G^\ddagger$ is the same at both temperatures. Thus, the exchange rate of proton and hydride in
[\text{Bu}^t\text{MoH(NH)}^+] is greater than that of [\text{Ph}^t\text{MoH(NH)}]^+ but less than that of [\text{Bu}^t\text{MoH(NH)}^+].

We expect the rate of the analogous Mo complex bearing a more basic amine would be slower. Indeed, variable-temperature 1H NMR spectra of [\text{Bu}^t\text{MoH(NH)}], with electron-donating 1Bu groups on the amine, shows that it has a slower proton-hydride exchange rate than [\text{Bu}^t\text{MoH(NH)}^+]. The individual resonances for amine-bound proton at 6.05 ppm and Mo hydride at 7.24 ppm were observed in the range between \(-70°\) and 10° in the 1H NMR spectrum in THF-d6. The decaolecence temperature of 20° is higher than that of [\text{Bu}^t\text{MoH(NH)}^+] (0° C), and the averaging Mo-H/N-H resonance of [\text{Bu}^t\text{MoH(NH)}^+] is not observed even at 100° C (Figure S65). The rate of exchanging proton and hydride at 25° C was measured as \(k = 2.1 \times 10^3\) s\(^{-1}\) (in THF) and 3.8 \(\times 10^1\) s\(^{-1}\) (in CDCl3), about 30 times slower than that of [\text{Bu}^t\text{MoH(NH)}].

The rates of proton-hydride exchange measured by dynamic 1H NMR spectroscopy give the following order: [\text{Ph}^t\text{MoH(NH)}] > [\text{Bu}^t\text{MoH(NH)}] > [\text{Bu}^t\text{MoH(NH)}^+] > [\text{Bu}^t\text{MoH(NH)}^+]. The rate of exchanging proton and hydride in [\text{Ph}^t\text{MoH(NH)}^+] is the fastest among this series of Mo-based heterolytic H\(_2\) cleavage products, because the relative acidities are very similar for the heterolytic cleavage complex and [\text{Ph}^t\text{MoH(NH)}^+] and the dihydrogen complex [\text{Ph}^t\text{Mo}(H_2)]. Complexes bearing more basic amines have lower acidity of the protonated amine, and the more electron-rich 1Bu on the phosphine decreases the acidity of dihydrogen/ dihydrogen ligand in the intermediate [\text{RR Mo(H)}]. In both cases, the higher pK\(_a\) values of the protonated amine in [\text{RR MoH(NH)}] and dihydrogen/dihydrogen ligand in [\text{RR Mo(H)}] result in a slower rate of exchange between the proton and hydride.

Measurement of the pK\(_a\) Values of [\text{RR MoH(NH)}]^+

Complexes in CD\(_2\)CN. The pK\(_a\) values of [\text{RR MoH(NH)}]^+ were determined in CD\(_2\)CN by 1H and 31P NMR spectroscopy. The pK\(_a\) of [\text{Ph}^t\text{MoH(NH)}]^+ in CD\(_2\)CN was determined relative to 2-methylpyridine (pK\(_a\) = 13.52 for the conjugate acid, 2-methylpyridinium) and 1,3,5-trimethylpyridine (pK\(_a\) = 14.98 for the conjugate acid). In the 1H NMR spectra, the aromatic resonances for each substituted pyridinium and pyridine coalesced into average resonances, and the Cp resonances for [\text{Ph}^t\text{MoH(NH)}] and \text{Ph}^t\text{MoH} also coalesced into one resonance, indicating fast exchange. Thus, the ratio of substituted pyridinium to pyridine for the pK\(_a\) reference and the analogous ratio for [\text{Ph}^t\text{MoH(NH)}] and \text{Ph}^t\text{MoH} were both determined from the weighted averages of the chemical shifts. Using these ratios, the equilibrium constant K\(_a\) was determined, and a pK\(_a\) of 13.8 ± 0.2 was obtained from the equation in Scheme 7. The pK\(_a\) value was also verified by addition of 2,6-lutidinium (pK\(_a\) = 14.13) into a CD\(_2\)CN solution of \text{Ph}^t\text{MoH} to attain equilibrium from the reverse direction.

The pK\(_a\) values of [\text{Ph}^t\text{MoH(NH)}], [\text{Bu}^t\text{MoH(NH)}], [\text{Bu}^t\text{MoH(NH)}^+], and [\text{Bu}^t\text{MoH(NH)}^+] in CD\(_2\)CN were determined as 9.3 ± 0.1, 10.7 ± 0.2, 13.5 ± 0.1, and 17.7 ± 0.1 by equilibration of 4-bromoaoline (pK\(_a\) = 9.43 for the conjugate acid), aniline (pK\(_a\) = 10.62 for anilinium), 1,3,5-trimethylpyridine, and benzylamine (pK\(_a\) = 16.91 for the conjugate acid), respectively. All of these pK\(_a\) data are averaged values from multiple measurements. The pK\(_a\) values (9.3–17.7) of these Mo complexes are lower than those of [\text{Cp}^{\text{C_{5}F_{4}}\text{Fe}(\text{H})\text{(P}^{\text{Bu}}\text{Bu}^{2}\text{H})]^+} and [\text{Cp}^{\text{C_{5}F_{4}}\text{Fe}(\text{H})(\text{P}^{\text{Bu}}\text{Bu}^{2}\text{N})]^+ (estimated as 20.7 and 18.3, respectively), which presumably results from the different electronic structure of the metals (d\(^4\) for Mo\(_0\) and d\(^5\) for Fe\(_0\)) as well as the additional \(\pi\)-acid CO ligand in the Mo complexes. 67

Scheme 7. Determination of the pK\(_a\) of Heterolytic H\(_2\) Cleavage Products

\[ pK_{a}(\text{Bu}^t\text{MoH(NH)}) = pK_{a}(H^+) - \log(K_{eq}) \]

DISCUSSION

The cleavage of H\(_2\) and the catalytic hydrogenation of unsaturated compounds have been extensively reported in main group systems since the pioneering work by Stephan, Erker, and their co-workers. 15–20 Heterolytic cleavage of H\(_2\) by transition-metal based frustrated Lewis pairs have been reported. Wass and co-workers reported H\(_2\) splitting by the cationic zirconium complex [\text{Cp}^{*}\text{ZrOCuH_3PBu}_2]^+ under mild conditions.29,30 Erker and co-workers developed a cationic zirconocene-amine complex, [\text{Cp}^{*}\text{Zr}(\text{OCH}_3\text{CH}_2\text{NPPr}_2)]\(^+\), for heterolytic cleavage of H\(_2\) and catalytic hydrogenation of alkenes.34 The H\(_2\) cleavage in both of these frustrated Lewis
A reactive vacant coordination site is crucial for H\textsubscript{2} binding and kinetics of H\textsubscript{2} addition to [Cp\textsubscript{2}ZrOC\textsubscript{6}H\textsubscript{4}PPr\textsubscript{2}]\textsuperscript{+}. For example, Wass and co-workers reported that the heterolytic cleavage of H\textsubscript{2} involving aromatization of pyridine-based pincer ligands, Milstein and co-workers used and basic centers, similar to that in main group Lewis pairs.\textsuperscript{86,87} Heterolytic cleavage of H\textsubscript{2} across iridium amide bonds.\textsuperscript{92} We propose that heterolytic cleavage of H\textsubscript{2} by Mo complexes \([\text{Mo}(\text{CO})_2(\text{PNP})]^{2+}\) occurs through a metal—ligand cooperation mechanism\textsuperscript{38–41} involving reaction of H\textsubscript{2} with the metal, forming the dihydride \(\text{M}(\text{H})_2\)\textsuperscript{+} or dihydrogen \(\text{M}(\eta^2\text{H}_2)\)\textsuperscript{+} complexes, followed by ligand-mediated intramolecular proton transfer to generate a protonated amine and a metal hydride. Heterolytic cleavage of H\textsubscript{2} by many other metal complexes also proceeds by similar mechanisms, such as iron complexes developed by Casey and Guan,\textsuperscript{7,44} and the iridium complexes with hydroxyl-substituted bipyridine ligands reported by Fujita and co-workers.\textsuperscript{88,89} A metal can also act as the base to promote inter- or intramolecular proton transfer in H\textsubscript{2} cleavage by some bimetallic complexes.

In the broader context of addition of H\textsubscript{2} across M–N bonds, Fryzuk and co-workers discovered early examples of the heterolytic cleavage of H\textsubscript{2} across iridium amide bonds.\textsuperscript{92} More recently, Grützmacher and co-workers found rhodium amide bonds that heterolytically cleave H\textsubscript{2}.\textsuperscript{93} Cooperative ligand reactivity was observed by Schneider and co-workers in the heterolytic cleavage of H\textsubscript{2} in a ruthenium nitride complex,\textsuperscript{94} leading to hydrogenolysis of the nitride and producing ammonia.\textsuperscript{14} In ruthenium\textsuperscript{95,96} and iridium\textsuperscript{97} complexes with pyridine-based pincer ligands, Milstein and co-workers used heterolytic cleavage of H\textsubscript{2} involving aromatization—dearomatization of the ligand as a key step in catalytic reactions exhibiting a wide scope of reactivity, with many examples documenting the formation of C–H bonds on the ligand. Heterolytic cleavage of H\textsubscript{2} is proposed in Fe complexes,\textsuperscript{98} including Fe complexes that catalyze the dehydrogenation of formic acid.\textsuperscript{99}

In transition-metal based FLPs and metal—ligand bifunctional complexes, the reactivity with H\textsubscript{2} can be altered by Lewis acid—base binding or by changing the electronic or steric characteristics of the coordination environment. The ability of the coordinated Lewis acid—base to dissociate and release the “unquenched” reactive vacant coordination site is crucial for H\textsubscript{2} binding and activation. For example, Wass and co-workers reported that the kinetics of H\textsubscript{2} addition to \([\text{CpP}^*\text{ZrOC}_{6}\text{H}_4\text{PR}_2]\)\textsuperscript{+} (R = \text{Pr}, \text{Mes}) complexes depends on the size of the substituents on zirconium and the phosphine.\textsuperscript{29,30} Though \([\text{Cp}^*\text{ZrOC}_6\text{H}_4\text{P}^*\text{Bu}_2]\)\textsuperscript{+} shows no Zr–P interaction and readily adds H\textsubscript{2}, \([\text{Cp}^*\text{ZrOC}_6\text{H}_4\text{P}^*\text{Bu}_2]\)\textsuperscript{+}, bearing the less sterically demanding Cp ligand, has a Zr–P bond and does not react with H\textsubscript{2}, similar to the lack of H\textsubscript{2} addition reactivity of \([\text{CpMo(CO)}(\eta^3\text{PNP})]\)\textsuperscript{+} because of the strong Mo–N coordination.

In our results, the additional ring strain in \([\text{CpMo(CO)}(\eta^3\text{P}_3\text{N})]\)\textsuperscript{+} (\([\text{RRMo}]^{+}\)) compared to \([\text{CpMo(CO)}(\eta^3\text{P}_3\text{NMepR}^3)]^{+}\) promotes the dissociation of Mo–N bond and enables H\textsubscript{2} addition. van Leeuwen and co-workers found that the steric effect of a pyridine ring in \([\text{diphosphine}](\text{Zr}(\eta^2\text{diphenylphosphino})-\text{pyridine})]\textsuperscript{2+} complexes has a significant impact on the activity for heterolytic cleavage of H\textsubscript{2}.\textsuperscript{100} The Pd complex bearing a methyl on the 6-position of pyridine ring shows much higher reactivity toward H\textsubscript{2} than that of the complex bearing an unsubstituted pyridyl group, probably because the 6-methyl group promotes the dissociation of the pyridyl group. All of these results demonstrate that H\textsubscript{2} cleavage reactivity in both transition-metal based FLPs and metal—ligand bifunctional complexes can be tuned by modulating the Lewis acid—base binding.

Short proton-hydride distances in some of these metal complexes have been revealed by NMR spectroscopy\textsuperscript{101–106} or by neutron diffraction in one example.\textsuperscript{66} In only a few cases were the proton-hydride exchange rates experimentally measured. Szymczak and co-workers reported that the doubly deprotonated ruthenium complex heterolytically cleaves H\textsubscript{2} via cooperation of metal and pendant oxyl groups, affording 3 as a ruthenium hydride complexes bearing two phenolic hydroxy groups (Figure 9).\textsuperscript{107} Complex 3 also shows dynamic exchange of two protons and one hydride, and its exchange rate was measured by spin-saturation transfer, corresponding to an

![Figure 8. Correlation between the pK\textsubscript{a} in CD\textsubscript{3}CN and proton/hydride exchange rates (k) in CD\textsubscript{2}Cl\textsubscript{2} at 25 °C. Triangles show the two complexes whose exchange rates were estimated from the dynamic NMR studies for the complexes formed from HD at low temperature in CD\textsubscript{2}Cl\textsubscript{2}, and squares indicate the three complexes whose exchange rates were determined by simulation of variable-temperature \textsuperscript{1}H NMR spectra in THF-d\textsubscript{4}.](Image 62x576 to 299x749)

![Figure 9. Metal complexes formed by heterolytic H\textsubscript{2} cleavage, and kinetics of exchange of the proton and hydride.](Image 351x89 to 537x364)
extrapolated rate of 519 s$^{-1}$ at 25 °C. This rate is about four times lower than that of $[^{1}t^{16}MoH(NH)]^{*}$ in THF-d$_{6}$ (2.1 × 10$^{3}$ s$^{-1}$). Both complex 3$^{107}$ and $[^{1}t^{16}MoH(NH)]^{*}$ have negative entropies of activation, $\sim 20 \pm 1$ cal K$^{-1}$ mol$^{-1}$ (in CD$_{2}$Cl$_{2}$) for 3 and $\sim 12.9 \pm 3.8$ cal K$^{-1}$ mol$^{-1}$ (in THF-d$_{6}$) for $[^{1}t^{16}MoH(NH)]^{*}$. A large negative $\Delta^{2}$ value would lead to a significant increase in $\Delta G^{2}$ at higher temperatures.

Andersen and Bergman reported Cp$^{*}_{5}$Ti(H)(SH) (4), which was generated from heterolytic cleavage of H$_{2}$ by Cp$^{*}_{5}$Ti=Sn.$^{108}$ The exchange dynamics of Ti–H and S–H resonances in Cp$^{*}_{5}$Ti(H)(SH) was measured by 2D EXSY 1H NMR spectroscopy, which gives an exchange rate of 1.2 s$^{-1}$ at $-30$ °C. DuBois and co-workers observed rapid proton-hydride exchange in [(P$^{2}$NMe$_{2}$H$^{2+}$)Fe(H)(dmpm) (CH$_{2}$CN)]$^{*}$ (5) and [(P$^{2}$NMe$_{2}$H$^{2+}$)Ni(H)(P$^{2}$NMe$_{2}$H$^{2+}$)]$^{*}$ (6) complexes, both bearing a di phosphine ligand with a pendant amine ligand.$^{63,64}$ The exchange rates for both complexes were estimated as $10^{4}$ s$^{-1}$ at 20 °C, corresponding to an activation barrier of 12 kcal/mol.

We developed manganese$^{97,90}$ and iron$^{65-67}$ complexes bearing pendant amines as electrocatalysts for oxidation of H$_{2}$. The Mn complexes have weak Mn–N bonds to the pendant amine that are readily displaced upon reaction with H$_{2}$ (1 atm), similar to the Mo–N bonds reported here. The iron complex [1]$^{*}$ and the manganese complex [2]$^{*}$ both show extremely rapid proton-hydride exchange dynamics at temperatures as low as $-80$ °C, with no decoalescence observed (Figure 9).$^{66,69}$ The exchange rates at low temperature for both complexes were estimated as $10^{4}$ s$^{-1}$ based on low-temperature NMR data for the complexes formed from HD. Rates over $10^{7}$ s$^{-1}$ at 25 °C were estimated, based on assumption that the $\Delta G^{2}$ is the same at 25 °C and $-80$ °C. The upper limits of the $\Delta G^{2}$ for both complexes are around 7 kcal/mol. The averaging proton-hydride resonance in the manganese complex [(P$^{2}$NMe$_{2}$H$^{2+}$)Fe(H)(dmpm) (CH$_{2}$CN)]$^{*}$ (7) bears a PNP ligand, reaches decoalescence at $-42$ °C.$^{70}$ A much slower exchange rate of 9.7 × 10$^{3}$ s$^{-1}$ at 20 °C and a higher $\Delta G^{2}$ of 11.8(8) kcal/mol at 25 °C, showing the positioning of amine and the ring flip conformational change, have a large impact on the dynamics of proton-hydride exchange. However, in most of the results mentioned above, only one or two complexes are reported; tuning the kinetics of proton-hydride exchange dynamics has not been extensively studied. Our results include the systematic measurement of thermodynamic and kinetic parameters of a series of Mo complexes as heterolytic H$_{2}$ cleavage products and demonstrate how to tune the kinetics of proton-hydride exchange dynamics.

The exchange rates of those complexes by simulation of the variable-temperature 1H NMR spectra. The trend of the decoalescence temperature for the averaging proton and hydride from the lowest to the highest of the five Mo complexes in CD$_{2}$Cl$_{2}$ again indicates the exchange rates from the highest to the lowest as $[^{Pb}{}^{Ph}{}^{Ph}MoH(NH)]^{*}$ > $[^{Pb}{}^{Ph}MoH(NH)]^{*}$ > $[^{Pb}{}^{Bu}MoH(NH)]^{*}$ > $[^{Bu}{}^{Bu}MoH(NH)]^{*}$ > $[^{Bu}{}^{Bu}MoH(NH)]^{*}$, which corresponds to the order of experimentally determined pK$_{a}$ values from the lowest to the highest.

■ CONCLUSIONS

Heterolytic cleavage of H$_{2}$ into a proton and a hydride was achieved in a series of Mo bifunctional complexes, [CpMo(CO)(κ$^{2}$-P$_{2}$-NR$^{2}$)$_{2}$]$^{*}$ [([RR]Mo)$^{*}$]. The exchange dynamics of proton and hydride in the complex showing fastest rate $[^{Pb}{}^{Ph}MoH(NH)]^{*}$, $10^{7}$ s$^{-1}$ at 25 °C, is nearly 10$^{4}$ times faster than that of the complex with slowest rate $[^{Bu}{}^{Bu}MoH(NH)]^{*}$, 2.1 × 10$^{3}$ s$^{-1}$, where we determined that the pK$_{a}$ values of five complexes [([RR]Mo)$^{*}$] in acetonitrile range from 9.3 to 17.7, leading to a quantitative understanding of how the proton-hydride exchange dynamics are controlled by the pK$_{a}$ of the complexes. A more basic amine or a more electron-donating phosphine leads to complexes with a lower acidity and a slower proton-hydride exchange rate. Our investigation into the relation between acidity and kinetic characteristics of bifunctional complexes provides design principles for the rational design FLPs for heterolytic cleavage of H$_{2}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b03053.

Experimental procedures, synthesis, variable-temperature 1-D and 2-D NMR spectroscopic data for all new compounds, measurement of $T_{1}$ relaxation time, and pK$_{a}$ determinations by 1H NMR spectroscopy (PDF)

X-ray crystallographic data (CIF)

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Notes

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■ REFERENCES


(82) The exchange rate for this coalescencing system is $ν = 2^{-1/2}(Δν)$, where $Δν$ is the separation of the Mo–H and N–H resonances.


