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Protonation Studies of a Tungsten Dinitrogen Complex Supported by a Diphosphine Ligand Containing a Pendant Amine

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Supporting Information

ABSTRACT: Treatment of $trans-[W(N_2)_2(dppe)-(P^{Et}N^{Me}P^{Et})]$ (dppe = Ph₂PCH₂CH₂PPh₂; $P^{Et}N^{Me}P^{Et}$ = Et₂PCH₂N(Me)CH₂PEt₂) with 3 equiv of tetrafluoroboric acid (HBF₄·Et₂O) at -78 °C generated the seven-coordinate tungsten hydride *trans*-[W(N_2)_2(H)(dppe)(P^{Et}N^{Me}P^{Et})][BF_4]. At higher temperatures, protonation of a pendant amine is also observed, affording *trans*-[W(N_2)_2(H)(dppe)(P^{Et}N^{Me}(H)-P^{Et})][BF_4]_2, with formation of the hydrazido complex [W(NNH₂)(dppe)(P^{Et}N^{Me}(H)P^{Et})][BF_4]_2 as a minor product. A similar product mixture was obtained using triflic acid (HOTf). The protonated products are thermally sensitive and do not persist at ambient temperature. Upon acid addition to



the carbonyl analogue *cis*- $[W(CO)_2(dpp)(P^{Et}N^{Me}P^{Et})]$, the seven-coordinate carbonyl hydride complex *trans*- $[W(CO)_2(H)-(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf]_2$ was generated. A mixed diphosphine complex without the pendant amine in the ligand backbone, *trans*- $[W(N_2)_2(dppe)(depp)]$ (depp = $Et_2P(CH_2)_3PEt_2$), was synthesized and treated with HOTf, selectively generating a hydrazido complex, $[W(NNH_2)(OTf)(dppe)(depp)][OTf]$. Computational analysis probed the proton affinity of three sites of protonation in these complexes: the metal, pendant amine, and N₂ ligand. Room-temperature reactions with 100 equiv of HOTf produced NH₄⁺ from reduction of the N₂ ligand (electrons come from W). The addition of 100 equiv of HOTf to *trans*- $[W(N_2)_2(dppe)(P^{Et}N^{Me}P^{Et})]$ afforded 0.81 equiv of NH₄⁺, while 0.40 equiv of NH₄⁺ was formed upon treatment of *trans*- $[W(N_2)_2(dppe)(depp)]$ with HOTf, showing that the complexes containing proton relays produce more products of reduction of N₂.

INTRODUCTION

Catalytic reduction of N_2 to ammonia using molecular complexes has been a longstanding goal that has challenged chemists for more than four decades. The importance of this transformation is evident when considering how the industrial method for ammonia synthesis (Haber–Bosch process) has accelerated production of NH_3 as an agricultural feedstock, resulting in dramatic human population growth in the last century.¹ In contrast with the energy-intensive conditions (high temperatures and pressures) used in the Haber–Bosch process, nitrogenase enzymes convert N_2 to ammonia under ambient conditions using a combination of protons and electrons at the structurally complex iron–molybdenum cofactor (FeMoco) active site² shown in Figure 1.

Deciphering the mechanism of N_2 reduction by nitrogenase enzymes remains the subject of intense investigation.³ Synthetic transition-metal dinitrogen complexes have served as means to investigate N_2 reactivity under mild conditions using protons and electrons.⁴ Additionally, structural models of the proposed N_2 binding site in FeMoco⁵ and investigations of proposed metal-bound intermediates⁶ along the N_2 reduction pathway



Figure 1. Structure of the iron-molybdenum cofactor (FeMoco) of nitrogenase.

have helped to understand this challenging chemical transformation.

Three examples of molecular catalysts for N_2 reduction with protons and electrons have been reported. The groups of Schrock⁷ and Nishibayashi⁸ developed Mo-based systems, and recently an Fe complex capable of catalytically reducing N_2 to ammonia was reported from the group of Peters.⁹ Importantly, each catalytic system operates optimally under a specific set of reaction conditions to achieve the maximum number of catalyst turnovers. Moreover, the steric and electronic features of the

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supporting ligand scaffold play a decisive role in producing an active catalyst that can convert N₂ to ammonia. In this context, a variety of innovative ligand design strategies have been implemented to produce low-valent group 6 dinitrogen complexes, $M(N_2)_2(P-P)_2$ (M = Mo, W; P-P = diphosphine ligand), one of the most extensively examined structure types investigated for the reduction of N_2 to ammonia.^{4b,10} For example, Nishibayashi and co-workers reported the complexes of the type $M(N_2)_2(P-P)_2$, supported by bidentate metallocene-containing diphosphine ligands (M = Mo, W; P-P = 1,1'-bis(diethylphosphino)ferrocene (depf),¹¹ 1,1'-bis(diethylphosphino)ruthenocene (depr),¹² bis(diethylphosphino-benzene)chromium (bepc)).¹³ Treatment of these dinitrogen complexes with sulfuric acid in methanol resulted in the formation of ammonia in good yield. This result is in contrast with the acid reactivity of complexes bearing traditional diphosphine ligands such as $M(N_2)_2(dppe)_2$ (M = Mo, W), which did not produce ammonia,¹⁴ further emphasizing the importance of the supporting ligand in facilitating protonation and reduction of the N₂ ligand.

We recently reported a series of Mo and W-N₂ complexes supported by diphosphine ligands containing noncoordinating pendant amine groups in the second coordination sphere.¹⁵ Introduction of a ligand scaffold containing the pendant bases represented a strategy aimed at regulating proton movement to facilitate the reduction of N2 to ammonia. Pendant amines have been shown to have a large influence on the catalytic rates in electrocatalytic reduction of protons to give H2.16 Herein we focus our efforts on understanding the reactivity of the pendant amine containing $W-N_2$ complex trans- $[W(N_2)_2(dppe) (P^{Et}N^{Me}P^{Et})]$ upon treatment with protic reagents such as HBF₄·Et₂O and HOTf. In this report, we describe the protonated products formed in these reactions, illustrating that the incorporation of this pendant methylamine group in the ligand backbone results in protonated products that differ from those of the complex bearing a traditional bidentate diphosphine ligand containing a hydrocarbon backbone. Furthermore, we demonstrate that treatment of the pendant amine-containing complex with 100 equiv of triflic acid produces twice the amount of ammonium than a complex bearing a traditional diphosphine ligand.

RESULTS AND DISCUSSION

Synthesis and Characterization of Tungsten N₂ Complexes. The preparation of group 6 dinitrogen complexes supported by one or two chelating phosphine ligands bearing pendant amines in the second coordination sphere have been reported for Cr,¹⁷ Mo,^{15,18} and W.^{15,18a} To understand how a pendant base in the second coordination sphere affects the reactivity patterns of the complexes upon addition of acid, in comparison to analogous systems bearing the conventional hydrocarbon-based ligand backbones, the mixed diphosphine complex *trans*-[W(N₂)₂(dppe)(P^{Et}N^{Me}P^{Et})]¹⁵ (1(N₂)₂) was prepared in THF by the reduction of W(dppe)Cl₄¹⁹ with magnesium powder in the presence of 1 equiv of P^{Et}N^{Me}P^{Et 20} under an N₂ atmosphere (eq 1).

The spectroscopic and structural characterization of $1(N_2)_2$ has been described in our earlier report.¹⁵ In this study, we focus on the reactivity of $1(N_2)_2$ because it contains electron-donating ethyl groups on the PNP ligand, resulting in an electron-rich metal center, thus enhancing the basicity of the coordinated N_2 ligands in comparison to analogues with electron-withdrawing phenyl substituents on the PNP ligand. In



addition, the effects on reactivity of the complex with acid due to the incorporation of only a single pendant amine functionality could be determined before a study on complexes bearing two PNP ligands is performed.¹⁵

To provide a direct comparison of the reactivity of $1(N_2)_{2J}$ a W-N₂ analogue without a pendant amine, trans-[W- $(N_2)_2(dppe)(depp)$ (2(N₂)₂), was prepared by the reduction of $W(dppe)Cl_4$ according to the reaction in eq 1. Here, the diphosphine ligand depp was employed due to its similarities in ring size, bite angle, and electronic characteristics to those of $P^{Et}N^{Me}P^{Et}$. The ³¹P NMR spectrum in THF-d₈ of the solution after reduction indicated that multiple products were produced, including $2(N_2)_2$, cis-[W(N_2)_2(dppe)(depp)], and minor products observed as singlets at δ 46.6 and -19.7 for trans- $[W(N_2)_2(dppe)_2]$ and *trans*- $[W(N_2)_2(depp)_2]$, respectively. We found that multiple extractions of the crude reaction mixture with pentane are necessary to obtain a pure sample of $2(N_2)_2$. The ³¹P NMR spectrum of $2(N_2)_2$ in THF- d_8 contains two multiplets at δ 43.9 and -16.3 for the dppe and depp ligands, respectively. Crystals suitable for X-ray diffraction were grown at room temperature by slow evaporation of an Et₂O/ THF mixture. The molecular structure of $2(N_2)_2$ is shown in Figure 2. Metric parameters for $2(N_2)_2$ are comparable to those



Figure 2. Molecular structure of $2(N_2)_2$. Thermal ellipsoids are drawn at the 50% probability level. Only the ipso carbons of the phenyl groups on the dppe ligand are shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)-W(1) = 2.4459(9), P(2)-W(1) = 2.4551(9), P(3)-W(1) = 2.4399(9), P(4)-W(1) = 2.4435(8), N(1)-W(1) = 2.033(3), N(3)-W(1) = 2.012(3), N(1)-N(2) = 1.095(4), N(3)-N(4) = 1.104(4); P(1)-W(1)-P(2) = 86.25(3), P(3)-W(1)-P(4) = 79.38(3), W(1)-N(1)-N(2) = 176.8(3), W(1)-N(3)-N(4) = 175.8(3), N(1)-W(1)-N(3) = 172.05(10).

of related $W(N_2)_2(diphosphine)_2$ complexes that have been structurally characterized,²¹ including those containing PNP ligands.¹⁵

Protonation Studies of *trans*-[W(N₂)₂(dppe)($P^{Et}N^{Me}P^{Et}$)] (1(N₂)₂) with HBF₄·Et₂O. The products generated upon the addition of 3 equiv of HBF₄·Et₂O to a CD₂Cl₂ solution of 1(N₂)₂ were dependent on the temperature of the reaction. For



Figure 3. Measured (top) and simulated (bottom) ${}^{31}P{}^{1}H$ NMR spectra of *trans*-[W(N₂)₂(H)(dppe)(P^{Et}N^{Me}P^{Et})][BF₄] ([3(N₂)₂]BF₄) recorded at -35 °C in CD₂Cl₂.

example, treatment of $1(N_2)_2$ with 3 equiv of HBF₄·Et₂O at -78 °C, when the reaction mixture was kept rigorously cold, formed the seven-coordinate tungsten bis(dinitrogen) hydride complex *trans*-[W(N₂)₂(H)(dppe)(P^{Et}N^{Me}P^{Et})][BF₄] ([3(N₂)₂]BF₄) (eq 2). The ³¹P NMR spectrum recorded at -35 °C contains four ddd resonances of equal intensity at δ 61.0, 34.7, -15.5, and -29.2 (Figure 3), indicating four inequivalent ³¹P environments. The ³¹P{¹H} coupling constants and the cross-peaks in the ³¹P-³¹P COSY NMR spectrum (see the Supporting Information) confirm that the four resonances belong to the same spin system.

The tungsten hydride resonance in the ¹H NMR spectrum appears as an apparent triplet of triplets (actually a ddd) at δ –3.76 (Figure 4). To confirm that $[3(N_2)_2]BF_4$ was protonated only at the metal center, the reaction was performed with a ¹⁵N-labeled amine in the PNP ligand, *trans*- $[W(N_2)_2(dppe)-(P^{Et}(^{15}N)^{Me}P^{Et})][BF_4]$ ($1(N_2)_2(^{15}N)$). The corresponding ¹⁵N{¹H} NMR spectrum of *trans*- $[W(N_2)_2(H)(dppe)-$



Figure 4. The hydride region of the ¹H NMR spectrum of $[3(N_2)_2]BF_4$ (bottom) and $[3(N_2)_2(NH)][BF_4]_2$ (top) recorded at -35 °C in CD_2Cl_2 .

 $(P^{Et}({}^{15}N)^{Me}P^{Et})][BF_4]$ ([3(N₂)₂(${}^{15}N)]BF_4$) contains a triplet at δ -362 (J_{NP} = 14 Hz) and does not exhibit ${}^{15}N$ -H coupling (typically ~80 Hz)^{22,23} in the proton-coupled ${}^{15}N$ NMR spectrum. Seven-coordinate transition-metal hydride bis-(dinitrogen) complexes have been reported for Mo and W supported by traditional chelating phosphine ligands (such as dppe) upon reaction with mineral acids such as HCl in methanol or THF, 14b,24 and additional details are described below.

Warming $[3(N_2)_2(^{15}N)]BF_4$ to 5 °C for several minutes and then returning the sample to -35 °C for data collection afforded the seven-coordinate hydride complex with a protonated pendant amine trans- $[W(N_2)_2(H)(dppe)_ (P^{Et}({}^{15}N)^{Me}(H)P^{Et})][BF_4]_2$ ([3(N₂)₂(${}^{15}NH)][BF_4]_2$). In this complex, the presence of a protonated pendant amine is evidenced by a doublet at δ –341 ($J_{\rm NH}$ = 79 Hz) in the protoncoupled ¹⁵N NMR spectrum. Furthermore, a cross peak in the $^{1}\text{H}^{-15}\text{N}$ HSQC NMR spectrum with a ^{15}N chemical shift at δ -341 correlating to a ¹H signal at δ 7.7 confirms the presence of the ¹⁵N-H bond. In the ³¹P NMR spectrum, resonances corresponding to the PNP ligand exhibit a significant shift downfield by ~13 ppm to δ –2.6 and –16.3 upon protonation of the pendant amine. The hydride reasonance of $[3(N_2)_2(^{15}NH)][BF_4]_2$ shifts slightly upfield to δ -4.3 (Figure 4) and is resolved into its component dddd ($J_{\rm PP}$ = 87.4, 75.4, 12.1, 8.9 Hz). A ¹⁵N{¹H} NMR spectrum of the ¹⁵N₂-labeled isotopologue $[3(^{15}N_2)_2(NH)][BF_4]_2$ exhibits resonances at δ -80 and -43 for the proximal and distal ¹⁵N atoms of the ¹⁵N₂ ligands, respectively. A cross-peak in the ¹H-¹⁵N HMBC NMR spectrum (¹⁵N, δ -80; ¹H, δ -3.7) shows that the hydride ligand is coupled to the proximal nitrogen atom of the coordinated ${}^{15}N_2$ ligand. $[3({}^{15}N_2)_2(NH)][BF_4]_2$ is unstable at room temperature. Warming the sample to 25 °C resulted in liberation of the dinitrogen ligands from the complex (a sharp singlet at δ -71 observed in the ¹⁵N NMR spectrum for liberated ¹⁵N₂) and the disappearance of the ³¹P NMR resonances, forming unidentified paramagnetic products.

Treatment of $[3(N_2)_2({}^{15}NH)][BF_4]_2$ with 20 equiv of Et₃N at -35 °C deprotonates the pendant amine of the PNP ligand, immediately regenerating $[3(N_2)_2]BF_4$ (eq 2). When the sample is warmed to 25 °C in the presence of 20 equiv of Et₃N, $[3(N_2)_2]BF_4$ is deprotonated at the metal center to regenerate $1(N_2)_2$. However, $1(N_2)_2$ is not stable in the presence of Et_3NH^+ , and over the course of ~30 min, due to N_2 loss, it converts to unidentified paramagnetic products on the basis of the absence of ³¹P NMR signals. In contrast, deprotonating $[3(N_2)_2(NH)][BF_4]_2$ with 100 equiv of Et₃N, followed by gradual warming to 25 °C, regenerates $1(N_2)_2$ as the only observed product by ³¹P NMR spectroscopy. In the presence of 100 equiv of Et_3N , $1(N_2)_2$ is stable for ~24 h at 25 °C. The large excess of base in solution clearly inhibits the transfer of protons to $1(N_2)_2$, which results in a thermally unstable product. The instability of $1(^{15}N_2)_2$ toward Et₃NH⁺ was examined independently, resulting in immediate liberation of N₂ ligands from tungsten (see the Supporting Information for details).

The protonation of $1(N_2)_2$ was investigated further by in situ IR spectroscopy by adding 3 equiv of HBF₄·Et₂O to $1(N_2)_2$ in CH₂Cl₂ at -40 °C. A plot of in situ IR spectra monitoring the $\nu_{\rm NN}$ bands of the starting material and products over the course of this reaction is shown in Figure 5. Upon addition of acid, the



Figure 5. In situ IR plot recorded at -40 °C from the reaction of $1(N_2)_2$ with 3 equiv of HBF₄·Et₂O in CH₂Cl₂, followed by the addition of 20 equiv of Et₃N. The total reaction time was 150 min. Data were collected in 15 s increments. The IR plot was rendered with each slice being approximately 200 s.

 $\nu_{\rm NN}$ band at 1925 cm⁻¹ from the starting bis(dinitrogen) complex $1(N_2)_2$ immediately disappeared, and a new ν_{NN} band appeared at 1995 cm⁻¹, assigned to $[3(N_2)_2]BF_4$. The increase in the N_2 vibrational frequency of 70 cm⁻¹ upon protonation of the metal center clearly demonstrates the effect of decreased back-bonding to the dinitrogen ligand in the oxidized (formally W(II)) metal center. This band persists for less than 30 s before the next IR measurement is recorded and the appearance of a new $\nu_{\rm NN}$ band at 2017 cm⁻¹ corresponding to the tungsten hydride product with a protonated pendant amine, $[3(N_2)_2(NH)][BF_4]_2$. The higher energy shift by 22 cm⁻¹ of the $\nu_{\rm NN}$ band upon pendant amine protonation is primarily due to the electrostatic effect of increasing the positive charge of the molecule from a monocation to a dication. Similarly, a 25 cm⁻¹ shift of the $\nu_{\rm NN}$ band to higher energy was observed upon protonation of the pendant amine site in *trans*-[Fe(H)(N₂)- 25 $(P^{Et}N^{Me}P^{Et})(dmpm)^{+}$ (dmpm = $(CH_3)_2PCH_2P(CH_3)_2)$, while a 16 cm⁻¹ increase in the $\nu_{\rm NN}$ band was observed upon protonation of the pendant amine in cis-[Fe(H)(N₂)- $(P^{Et}N^{Me}P^{Et})_2]^+$.²⁶ The addition of 20 equiv of Et₃N immediately deprotonates the pendant amine site in $[3(N_2)_2(NH)][BF_4]_2$, resulting in a rapid shift of the 2017 cm⁻¹ band back to 1995 cm⁻¹. When the reaction mixture is warmed to 21 °C, the starting bis(dinitrogen) complex $1(N_2)_2$ is regenerated, indicated by the $\nu_{\rm NN}$ band at 1925 cm⁻¹. Over the course of 40 min, $1(N_2)_2$ slowly loses the bound N_2 ligands in the presence of Et₃NH⁺, consistent with N₂ loss and conversion of $1(N_2)_2$ into unidentified paramagnetic products observed by NMR (vide supra). In an attempt to observe the complex that is only protonated at the pendant amine, trans- $[W(N_2)_2(dppe)(P^{Et}N^{Me}(H)P^{Et})][BF_4]$, in situ IR spectra were collected at a rate of 5 scans/s. However, even at the faster rate of data collection, this product was not detected in the in situ IR spectrum. This observation suggests that the metal center is protonated directly or that the rate of intramolecular proton transfer from the hypothesized protonated pendant amine to the metal center is too rapid to be observed under these conditions.

In the reactions described above, $[3(N_2)_2]BF_4$ was generated when the reaction was kept rigorously cold during the initial addition of HBF₄·Et₂O to $1(N_2)_2$. Once $[3(N_2)_2]BF_4$ is formed, warming the solution to 5 °C afforded $[3(N_2)_2(NH)]$ - $[BF_4]_2$, where the pendant amine site of the PNP ligand is protonated. In contrast to this stepwise protonation (as a result of changing the reaction temperature), when a CD₂Cl₂ solution of $1(N_2)_2$ cooled to -78 °C is treated with 3 equiv of HBF₄. Et₂O and the solution is warmed briefly²⁷ during the initial sample mixing, before inserting into the NMR probe maintained at -35 °C, a different mixture of protonated products is obtained, shown in eq 3. Under these conditions,



the ³¹P NMR spectral data indicated the formation of $[3(N_2)_2(NH)][BF_4]_{22}$ which accounted for ~85% of the total phosphorus-containing products. A second protonated species accounting for the remaining ~15% of the total products was identified as the hydrazido complex *trans*- $[W(NNH_2)(F)-(dppe)(P^{Et}N^{Me}(H)P^{Et})][BF_4]_2$ ($[1(NNH_2)(F)(NH)][BF_4]_2$) (see the Supporting Information). The ³¹P resonances assigned to $[1(NNH_2)(F)(NH)][BF_4]_2$ include a pair of doublet of doublets at δ 35.4 and 10.9, due to ³¹P-³¹P and ³¹P-¹⁹F coupling (~40-50 Hz).^{22,23,28}

A multiplet in the ¹⁹F NMR spectrum at δ –187 corresponds to the tungsten fluoride resonance. The ¹H–¹⁵N HSQC NMR spectrum, using the ¹⁵N₂-labeled complex [1(¹⁵N¹⁵NH₂)(F)-



Figure 6. ³¹P{¹H} NMR spectrum recorded at -40 °C in CD₂Cl₂ after 6 equiv of HOTf was added to $1({}^{15}N_2)$. Two major products observed were observed: (black) *trans*-[W({}^{15}N_2)_2(H)(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf]_2 ([$3({}^{15}N_2)_2(NH)$][OTf]₂); (blue) *trans*-[W({}^{15}N^{15}NH_2)(OTf)(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf]_2 ([$1({}^{15}N^{15}NH_2)(OTf)(NH)$][OTf]₂). The identity of the minor product with resonances at δ 43.7 and 7.5 has not been determined.

 $(NH)][BF_4]_2$, exhibits a cross peak for the protonated distal nitrogen atom of the hydrazido ligand with a ^{15}N chemical shift at δ -46 and a corresponding ¹H resonance at δ 5.60. Accordingly, in the ¹H NMR spectrum, a doublet at δ 5.63 ($J_{\rm HN}$ = 80.0 Hz) is assigned as the protons of the hydrazido ligand. This resonance is a broad singlet in the W-14N14NH2 isotopologue. Performing the reaction with a ¹⁵N-labeled pendant amine, $1(N_2)_2(^{15}N)$, upon generation of $[1(NNH_2) (F)({}^{15}NH)][BF_4]_2$ two cross peaks are observed in the ${}^{1}H-{}^{15}N$ HSQC NMR spectrum with ¹H NMR signals at δ 10.37 and 10.55, with a ¹⁵N NMR chemical shift of δ –341. These signals are assigned as two possible isomers of $[1(NNH_2)(F)(^{15}NH)]$ - $[BF_4]_2$ with the proton on the pendant amine positioned *endo* or exo with respect to the hydrazido group. The products generated in this reaction are thermally sensitive, and when the sample is warmed above 10 °C, it slowly converted to unidentified paramagnetic products. However, if the reaction is maintained at -35 °C, addition of 20 equiv of Et₃N converts $[1(NNH_2)(F)NH)][BF_4]_2$ to $1(N_2)_2$. Further warming to room temperature converts the remaining $[3(N_2)_2]BF_4$ back to $1(N_2)_2$ before eventual loss of ³¹P NMR signals. Precedent for deprotonation of the hydrazido groups comes from tungsten hydrazido complexes supported by diphosphine ligands such as trans- $[W(NNH_2)(p-MeC_6H_4SO_3)(dppe)_2]^+$ (without pendant amines) that have been deprotonated by $Et_3N^{24a,29}$ to regenerate the parent dinitrogen complex.

In a related study examining the reactivity of a pendant amine containing Mo bis(dinitrogen) complex with a strong acid, Tuczek and co-workers treated *trans*-[Mo(N₂)₂(dppe)-(pyNP₂)]^{18a} (pyNP₂ = *N*,*N*-bis(diphenylphosphinomethyl)-2-aminopyridine) with 3 equiv of HBF₄·Et₂O in CD₂Cl₂ at -15 °C, generating the hydrazido-containing product [Mo(NNH₂)-(F)(dppe)(pyN(H)P₂)][BF₄]₂.^{18b} In addition to protonation of the N₂ ligand, the pyridine group of the supporting pyNP₂ ligand was protonated, as determined from X-ray crystallographic data. Notably, while acid addition was performed at reduced temperature, the protonated product [Mo(NNH₂)-(F)(dppe)(pyN(H)P₂)][BF₄]₂ is thermally stable, in contrast to the thermally sensitive protonated tungsten products [1(NNH₂)(F)(NH)][BF₄]₂ and [3(N₂)₂(NH)][BF₄]₂ de-

scribed above. Factors that may influence the stability of the protonated products include the identity of the metal center and the electron-donating ability of the supporting phosphine ligands; thus, it is difficult to conclusively identify the reasons for the different stability of [Mo(NNH₂)(F)(dppe)(pyN(H)- P_2][BF₄]₂ in comparison to [1(NNH₂)(F)(NH)][BF₄]₂. While it is clear the pendant amine incorporated in the backbone of the ligand results in reactivity patterns different from those in the absence of the amine, the proximity of the pendant aminopyridine group with respect to the metal center and/or the hydrazido ligand and the basicity of the pendant group are important factors that could influence the stability of these products. In $1(N_2)_2$, the pendant amine is more basic than the distal nitrogen atom of the N2 ligand (vide infra), indicating that the transfer of a proton from a protonated pendant amine to the N2 ligand would be unfavorable. Because intramolecular proton transfer could occur from a protonated N_2 intermediate (such as the hydrazido species) to the pendant amine, the hydrazido complexes are not expected to form without a protonated pendant amine.

Reactivity of trans-[W(N2)2(dppe)(PEtNMePEt)] and trans-[W(N₂)₂(dppe)(depp)] with HOTf. In addition to the protonation studies with HBF₄·Et₂O, the reactivity of $1(N_2)_2$ with triflic acid (HOTf) was examined to determine if the identity of the counterion would influence the distribution of protonated products. A solution of $1({}^{15}N_2)_2$ in CD₂Cl₂ was treated with 6 equiv of HOTf at -78 °C before inserting into an NMR probe maintained at -40 °C, as shown in eq 4. In this reaction, despite conditions in which the NMR tube was kept rigorously cold during sample mixing, integration of the ³¹P NMR spectrum, shown in Figure 6, indicated ~81% conversion to trans- $[W(^{15}N_2)_2(H)(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf]_2$ $([3(^{15}N_2)_2(NH)][OTf]_2)$ and 18% conversion to trans-[W- $({}^{15}N{}^{15}NH_2)(OTf)(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf],$ $([1(^{15}N^{15}NH_2)(OTf)(NH)][OTf]_2)$. Multiplets at δ 63.7, 40.1, -0.2, and -13.6 correspond to the seven-coordinate W hydride, with their PNP ligand resonances shifted downfield, indicative of a protonated pendant amine as described above. In addition, multiplets at δ 35.4 and 2.7 ($J_{\rm PP}$ = 127 Hz) correspond to the hydrazido complex. The ¹H NMR spectrum



contains a dddd (apparent tt) at δ –4.32 for the W hydride resonance in $[3(^{15}N_2)_2(NH)][OTf]_2$, while the hydrazido resonance of $[1(^{15}N^{15}NH_2)(OTf)(NH)][OTf]_2$ appears as a doublet at δ 6.54 ($J_{NH} = 89$ Hz). The ¹⁵N chemical shifts of the proximal and distal N atoms in $[1(^{15}N^{15}NH_2)(OTf)(NH)]$ - $[OTf]_2$ and $[3(^{15}N_2)_2(NH)][OTf]_2$ are identical with those of complexes with the BF₄⁻ anion. Treatment of the products with 30 equiv of Et₃N at -40 °C deprotonated the pendant amine, forming $[3(^{15}N_2)_2]OTf$. Accordingly, the ³¹P resonances for the PNP ligand shift 11–13 ppm upfield as in the reactions with HBF₄·Et₂O described above. The pendant amine and hydrazido ligand in $[1(^{15}N^{15}NH_2)(OTf)(NH)][OTf]_2$ are also deprotonated, regenerating the starting dinitrogen complex $1(N_2)_2$. Warming the sample to room temperature results in loss of ³¹P NMR signals.

As noted above, complex $2(N_2)_2$ was prepared as an analogue to $1(N_2)_2$, in which the depp ligand replaces the pendant amine-containing PNP ligand. To provide a comparison of the reactivity studies with acid, a solution of $2(N_2)_2$ in CD₂Cl₂ was treated with 3 equiv of HOTf at -78 °C. ³¹P NMR spectral data collected at -40 °C shows conversion to the hydrazido product *trans*-[W(NNH₂)(OTf)(dppe)-(depp)][OTf] ([2(NNH₂)(OTf)][OTf]), (eq 5). Similarly,



the hydrazido product $[2(NNH_2)(F)][BF_4]$ was formed upon treatment of $2(N_2)_2$ with HBF₄·Et₂O. In contrast to the protonation studies with $1(N_2)_2$, no W hydride product was observed in these reactions, indicating that incorporation of the pendant amine in the second coordination sphere has a significant effect in promoting the protonation of the metal center. In addition, $[2(NNH_2)(OTf)][OTf]$ is more thermally robust than $[1(NNH_2)(OTf)(NH)][OTf]_2$ and does not convert into paramagnetic product upon warming to 22 °C.

Reactivity of a W(CO)₂ Analogue with [4-BrPhNH₃]-[**OTf].** To compare the preferred sites of protonation with $1(N_2)_2$ and to provide a comparison of NMR and IR spectroscopic data, the tungsten dicarbonyl analogue W- $(CO)_2(dppe)(P^{Et}({}^{15}N)^{Me}P^{Et})$ was treated with acid. The previously reported *cis*-dicarbonyl complex *cis*-[W- $(CO)_2(dppe)(P^{Et}({}^{15}N)^{Me}P^{Et})$] (*cis*-[$1(CO)_2({}^{15}N)$]) was synthesized by stirring a solution of $1(N_2)_2$ under an atmosphere of CO.¹⁵ The ${}^{13}CO$ -labeled complex *cis*-[W({}^{13}CO)_2(dppe)-(P^{Et}N^{Me}P^{Et})] (*cis*-[$1({}^{13}CO)_2$]) was prepared to provide additional spectroscopic information. For *cis*-[$1({}^{13}CO)_2$], two carbonyl resonances are identified in the ${}^{13}C\{{}^{1}H\}$ NMR spectrum at δ 221.0 and 218.7, while two $\nu_{^{13}CO}$ bands of equal

intensity are observed at 1792 and 1729 cm⁻¹ in the IR spectrum. These bands are shifted to lower frequency by approximately 45 cm⁻¹ in comparison to those in the ¹²CO sample. Treatment of *cis*-[1(CO)₂] with 3 equiv of 4-bromoanilinium triflate, [4-BrPhNH₃][OTf] (pK_a = 9.4 in acetonitrile³⁰), at room temperature results in an immediate color change from orange to yellow, as *trans*-[W(CO)₂(H)-(dppe)(P^{Et}(¹⁵N)^{Me}(H)P^{Et})][OTf]₂ ([3(CO)₂(¹⁵NH)][OTf]₂) is generated (eq 6). The IR spectrum (KBr) exhibits an intense



antisymmetric $\nu_{\rm CO}$ band at 1851 cm⁻¹ and a weak symmetric $\nu_{\rm CO}$ band at 1957 cm⁻¹, indicating a trans configuration of the CO ligands. Similar isomerization from a cis-dicarbonyl to a trans-dicarbonyl product upon protonation of the metal center was noted in molybdenum complexes without pendant amine containing ligands. For example, the conversion of cis- $[Mo(CO)_2(dmpe)_2]$ (dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$) to *trans*- $[Mo(H)(CO)_2(dmpe)_2]HCl_2$ has been reported upon the addition of HCl.³¹ In the present case, NMR spectral data corroborate the structural assignment from the IR data. A single carbonyl resonance is observed in the ${}^{13}C{}^{1}H$ NMR spectrum at δ 204.5 for the ¹³CO-labeled complex. The ¹H NMR spectrum identifies the tungsten hydride at δ -5.18. In addition, the pendant amine of the seven-coordinate dicarbonyl hydride complex is protonated, indicated by a doublet $(I_{\rm NH} =$ 76 Hz) in the ¹⁵N NMR spectrum at δ –338. The ³¹P{¹H} NMR spectrum of $[3(CO)_2(^{15}NH)]^{2+}$ contains four multiplets at δ 60.7, 43.6, -11.6, -23.4, indicating four distinct phosphorus environments. In a related study, the molecular structure of the molybdenum dicarbonyl complex trans- $[Mo(H)(CO)_2(dppe)_2]^+$ was determined by X-ray diffraction.³² Although the hydride ligand was not observed in the final difference map, the location of the hydride ligand was inferred to be located between chelating phosphine ligands on the P4 plane, on the basis of Mo-P bond angles. An analogous seven-coordinate structure is expected in the present case. Treatment of $[3(^{13}CO)_2(^{15}NH)][OTf]_2$ with 20 equiv of Et₃N at -40 °C formed a mixture of $cis-[1(^{13}CO)_2]$ and trans- $[W({}^{13}CO)_2(dppe)(P^{Et}N^{Me}P^{Et})]$ (trans- $[1({}^{13}CO)_2]$). When 10 equiv of Et₃N is added at 21 °C, only $cis-[1(^{13}CO)_2]$ is formed, thus, cis/trans isomerization is slow at reduced temperatures.

Computational Analysis. Computational analysis employing density functional theory (DFT) based electronic structure methods was used to augment the protonation studies of $1(N_2)_2$ and $2(N_2)_2$. An evaluation of the thermodynamically preferred protonation sites in these molecules was performed in order to (1) rationalize the products formed upon treatment of



Figure 7. Computationally derived proton affinity values in kcal/mol for the protonation of $1(N_2)_2$, $2(N_2)_2$, and $[3(N_2)_2]^+$.

with strong acids, (2) evaluate the effect of pendant amine protonation on N₂ binding, and (3) understand how to predict and control reactivity patterns to aid in the future design of new compounds. First, we examined the proton affinity of the proton-accepting sites on $1(N_2)_2$ (metal center, pendant amine, and N₂ ligand) in this computational assessment, shown in Figure 7. The proton affinity values for the single protonation of $1(N_2)_2$ in THF varied over a wide range. The electron-rich metal center was determined to have the highest proton affinity of 22.1 kcal/mol, followed by the pendant amine site of 10.4 kcal/mol. The proton affinity for the distal nitrogen of the dinitrogen ligand was considerably lower at 2.0 kcal/mol. For comparison, the proton affinity of the tungsten center and the N_2 ligand were determined for complex $2(N_2)_2$. As expected for complexes that are structurally and electronically similar, the calculated proton affinity values were nearly identical with those of $1(N_2)_2$ at 22.4 and 2.0 kcal/mol for the tungsten center and the dinitrogen ligand, respectively.

While the computational results indicate that the metal center is the thermodynamically favored protonation site in $1(N_2)_2$ and $2(N_2)_2$, the reactivity studies discussed above show that the formation of the seven-coordinate tungsten hydride product is observed in reactions with $1(N_2)_2$, but not with $2(N_2)_2$. Furthermore, despite the ~20 kcal/mol lower proton affinity value of the N2 ligand versus the metal center, only protonation at the N₂ ligand is observed with $2(N_2)_2$. The disparity in reactivity between the two complexes could be rationalized by the pendant amine and dinitrogen ligands being kinetically favored protonation sites upon acid addition, as a result of their location in the second coordination sphere. In the case of $1(N_2)_2$, initial protonation of the pendant amine may ultimately result in rapid intramolecular nitrogen to metal proton transfer to give the thermodynamically preferred product. In reactions with $2(N_2)_2$, the second protonation at the N₂ ligand, leading to the formation of a stable hydrazido product, may occur before protonation at the thermodynamically preferred metal center. No clear intermolecular pathway is accessible to transfer the proton to the metal center before the formation of the stable hydrazido product.33

It is important to note a related kinetic study by Henderson that reported a mechanism by which hydrazido and metal– hydrido complexes are formed upon addition of mineral acids (HX = HCl, HBr, H₂SO₄) to *trans*- $[M(N_2)_2(P-P)_2]$ (M = Mo, W; P–P = dppe, depe) in THF (depe = Et₂PCH₂CH₂PEt₂). Formation of $[W(N_2)_2(dppe)_2]$ HX, an adduct between HX and the metal complex, was suggested to be the initial product formed in the reaction with acid. In reactions with HCl, low acid concentrations favored the formation of the metal hydride product. Higher concentrations of acid resulted in formation of the hydrazido product. These results were rationalized by intramolecular electrophilic attack of HX on the metal (within the adduct) being faster at lower acid concentrations in comparison to protonation of the N_2 ligand by an additional 1 equiv of acid. This example demonstrates that a metal hydride product for complexes such as $2(N_2)_2$ can be generated under certain experimental conditions, which are likely dependent on the identity of the acid and the medium. However, under the conditions employed in the present study with $2(N_2)_2$, the W hydride product was not formed, indicating that the direct protonation of the metal center is not kinetically preferred.

A computational assessment of the proton-accepting sites of the seven-coordinate hydride complex $[3(N_2)_2]^+$ indicates a substantial shift in the pendant amine proton affinity to -1.9kcal/mol, while the dinitrogen ligand remains the least basic site, with a proton affinity of -20.4 kcal/mol. The dramatic shift in proton affinity values at these sites reflects the cationic charge of the hydride complex as well as a less electron donating metal center. Promoting additional protonation events at the N₂ ligand after the formation of the tungsten hydride complex is clearly disfavored on the basis of the more acidic nature of this site.

To investigate the W–N₂ binding strength in $1(N_2)_2$ and in potential (but not spectroscopically observed) structures containing a protonated pendant amine, the free energy for the dissociation of dinitrogen from tungsten was evaluated computationally. For $1(N_2)_2$, an N_2 dissociation free energy of 16.4 kcal/mol was predicted, indicating a moderately labile N₂ ligand in this low-valent complex. Experimental observations are in line with the predicted lability of the N₂ ligand, as substitution by CO (presumably through a dissociative mechanism) is slow, requiring $\sim 37-72$ h for complete conversion to the tungsten dicarbonyl complex described above.¹⁵ Upon protonation of the pendant amine, the N₂ dissociation free energy of the cationic species was slightly lower at 15.0 kcal/mol. The magnitude of the change in N₂ dissociation energy in the protonated species is consistent with our previously reported analysis for the protonation of a pendant amine site in trans- $[FeH(N_2)(P^{Et}N^{Me}P^{Et})(dmpm)]^+$. An electrostatic effect (increased positive charge) was determined to be the major contributing factor, resulting in a decrease of N₂ binding energy and an increase in the $\nu_{\rm NN}$ vibrational frequency. In the current study, IR spectroscopic data did not indicate the formation of a discrete complex formulated as trans- $[W(N_2)_2(dppe)(P^{Et}N^{Me}(H)P^{Et})]^+$, but the 22 cm⁻¹ shift between the hydride species $3(N_2)_2$ and $[3(N_2)_2(NH)]^{2+}$ indicates the trend in ν_{NN} vibrational frequency remains consistent between the Fe and W systems upon protonation of the pendant amine. Most importantly, however, is recognizing the protonation events that have the greatest impact toward reduction of the N2 ligand. Initial protonation of the pendant amine site lowers the proton affinity of the N₂ ligand and the N₂ dissociation energy to the metal

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center. Thus, directing the initial protonation at the N_2 ligand represents an important objective. In addition, modifications to the ligand design that include modulating the proximity of the amine with respect to the N_2 ligand and tuning the amine proton affinity to be more closely matched to the N_2 ligand may help avoid potential undesired intramolecular proton transfer and favor intramolecular transfer steps that lead to reduced N_2 products.

Protonolysis Reactions with Triflic Acid. To determine if the incorporation of a pendant amine in the second coordination sphere of the dinitrogen complex would result in NH_4^+ formation upon the addition of a significant excess of triflic acid, experiments examining this reactivity were performed on $1(N_2)_2$ and $2(N_2)_2$. Triflic acid was chosen because oxygen-containing anions have been suggested to be important in facilitating the reduction of N_2^{33} and to avoid coordination of fluoride ligand, which binds upon protonation with HBF₄·Et₂O.^{34,22,35} Treatment of an orange solution of $1(N_2)_2$ in CH₂Cl₂ at room temperature with 100 equiv of HOTf resulted in a pale orange solution. After the mixture was stirred for 20 h, the ammonium produced in the reaction was quantified using the indophenol method (see the Experimental Section for details). In reactions with $1(N_2)_2$, 0.81 equiv of ammonium was produced per metal center (eq 7). For



comparison, the addition of acid to an orange solution of $2(N_2)_2$ afforded a green solution and resulted in the formation of 0.40 equiv of ammonium per tungsten center. Thus, the pendant amine containing complex $1(N_2)_2$ produced twice as much ammonium as $2(N_2)_2$. Hydrazine was not detected as a product in either reaction. Two equivalents of ammonium is the theoretical yield without the addition of an external reductant, with the six d electrons in W(0) being the limiting reagent.

To confirm that the ammonium produced in this reaction resulted from reduction of the metal-bound N₂ ligand and not from the degradation of the pendant amine or from atmospheric N₂, the reaction was performed with the ¹⁵N₂-labeled isotopologue $1(^{15}N_2)_2$. Accordingly, ammonium was observed in the ¹H NMR spectrum as a doublet (¹⁵N: $I = \frac{1}{2}$) at δ 7.06 ($J_{\rm HN} = 72$ Hz) instead of a 1:1:1 triplet ($J_{\rm HN} = 51$ Hz, resulting from coupling to ¹⁴N (I = 1)), shown in Figure 8.

It is difficult to provide the exact reason for the higher yields of ammonium produced from $1(N_2)_2$. One possibility is that the pendant amine group plays a key role in promoting the formation of protonated N₂ intermediates past the hydrazido species, one of the most stable intermediates in the N₂ reduction pathway. An examination of the products at the end of the reactions with $2(N_2)_2$ showed the presence of the hydrazido complex $[2(NNH_2)(OTf)][OTf]$, indicating that a portion of this material did not proceed past this intermediate, thus failing to cleave the N–N bond. A hydrazido product was not observed at the end of the reactions with $1(N_2)_2$. In the case of $1(N_2)_2$, the greater positive charge (due to the protonated pendant amine) associated with a complex



Figure 8. ¹H NMR spectrum (top) from the addition of HOTf (100 equiv) to $1(N_2)_2$ in CH₂Cl₂ at 21 °C, resulting in the formation of NH₄⁺ as a 1:1:1 triplet ($J_{\rm HN}$ = 51 Hz) at δ 7.06 in DMSO- d_{6} . Repeating the experiment with $1(^{15}N_2)_2$ affords a doublet ($J_{\rm HN}$ = 72 Hz) (bottom).

containing a hydrazido intermediate would exhibit a more positive reduction potential, which could help promote intermolecular electron transfer reactions to aid N2 reduction. $^{25,18\mathrm{a}}$ Proton transfer to the N_2 ligand could follow or occur concomitantly with the electron transfer step. Although formation of the seven-coordinate tungsten hydride complex appears to be detrimental toward facilitating protonation and reduction of the N₂ ligand, in a related mechanistic study by Henderson, the initial protonation of *trans*- $[Mo(N_2)_2(depe)_2]$ with HCl in THF resulted in the formation of $Mo(H)(N_2)$ - $(Cl)(depe)_2$ upon loss of one N₂ ligand.^{24b} Although the initial protonation did not occur at the N₂ ligand, this study proposed that subsequent formation of *trans*-[Mo(NNH₂)(Cl)(depe)₂]⁺ could proceed through the initially formed Mo-H complex by an acid-catalyzed pathway. In addition, metal hydrides have been shown to play an important role in a variety of systems for N₂ reduction to ammonia.³⁶ Relevant examples include intermediate states formed during catalytic turnover of the nitrogenase enzyme, silica-bound transition-metal-containing heterogeneous systems, and a variety of synthetic homogeneous complexes.³⁶ In the present case, preferential formation of the W-H complex is apparent in reactions of $1(N_2)_2$ with stoichiometric amounts of acid. It is unclear at this time whether the W-H product plays a role in the protonolysis reactions, resulting in higher yields of NH4⁺ in comparison to those for complex $2(N_2)_{2}$, where the formation of a W-H product is not observed. Studies are underway to understand the effect of the pendant amine and the transition-metal hydride complexes in promoting NH₄⁺ production.

CONCLUSIONS

We examined the reactivity of a tungsten bis(dinitrogen) complex supported by a PNP ligand containing a pendant methyl amine in the ligand backbone as a strategy for regulating proton movement in the second coordination sphere to facilitate the reduction of N₂ to ammonia. The reactivity of $1(N_2)_2$ and a structural analogue containing a hydrocarbon backbone, $2(N_2)_2$, toward protic reagents such as HBF₄·Et₂O and triflic acid at low temperature led to an understanding of the reactivity patterns of these complexes. Our results demonstrate that the incorporation of the pendant amine group in the ligand backbone affords the seven-coordinate tungsten hydride complex $[3(N_2)_2(NH)]^{2+}$ as the major product. Protonation of the N₂ ligand formed the tungsten

hydrazido complex $[1(NNH_2)(X)(NH)]^{2+}$ (X = F, OTf), observed as a minor product. Analogous reactions with $2(N_2)_2$ formed the W hydrazido complex $[2(NNH_2)(X)]^+$ (X = F, OTf) without the formation of a tungsten hydride product. Importantly, in protonolysis reactions with excess triflic acid, the complex containing the PNP ligand produced twice the amount of ammonium in comparison to the complex with the depp ligand. These results indicate that the incorporation of a basic pendant amine in the ligand backbone of the dinitrogen complex significantly influences the formation of reduced N₂ intermediates, such as a hydrazido species, that are commonly generated as stable products in complexes such as $2(N_2)_2$. While the amine-containing complex $1(N_2)_2$ clearly favors the formation of the seven-coordinate hydride product in reactions with stoichiometric amounts of acid, the role of the amine in enhancing the formation of ammonia in the presence of excess acid is unclear at this time. In light of this encouraging result, future work will examine the reactivity of group 6 dinitrogen complexes containing less basic pendant amine substituents to more closely match the amine basicity to that of the dinitrogen ligand. Moreover, an understanding of how to utilize the pendant bases to control proton movement and delivery to the N2 ligand to facilitate ammonia formation will be of great utility toward the goal of developing electrocatalytic N2 reduction systems in our laboratory.

EXPERIMENTAL SECTION

General Experimental Procedures. All synthetic procedures were performed under dry N2 or argon using standard Schlenk techniques or a glovebox. Protio solvents were purchased as anhydrous, dried by passage through activated alumina columns in a solvent purification system, and stored under N2 or argon until use. Benzene-d₆ and THF-d₈ were dried over Na/K and degassed under high vacuum (10^{-6} Torr) before being distilled and stored under N₂ until use. CD2Cl2 was dried over CaH2. DMSO-d6 was used as received. All reagents were purchased from commercial sources and used as received. Triethylamine was degassed under vacuum and dried over 3 Å molecular sieves before use. The ¹H, ¹³C, ¹⁵N, and ³¹P NMR spectra were collected on a 500 MHz spectrometer at ambient temperature unless otherwise indicated. ¹H and ¹³C NMR chemical shifts are referenced against tetramethylsilane using internal solvent resonances. ³¹P NMR chemical shifts are proton decoupled unless otherwise noted and referenced to H3PO4 as an external reference. ¹⁵N NMR chemical shifts were referenced to $CH_3^{15}NO_2$ ($\delta 0$). Phosphorus coupling to the ¹⁸³W nuclei was not included in the simulations of the ³¹P NMR spectra. Infrared spectra were recorded as a KBr pellet under a purge stream of nitrogen gas. In situ IR experiments were recorded on a Mettler-Toledo ReactIR 15 spectrometer equipped with a liquid nitrogen cooled MCT detector, connected to a 1.5 m AgX Fiber DS series (9.5 mm \times 203 mm) probe with a silicon sensor. Experiments were performed in a 5 or 10 mL two-neck pear-shaped flask under a dinitrogen atmosphere. IR spectra were collected in intervals of 15 s in the normal collection mode or in "rapid collect" mode at a rate of five scans per second. In situ IR experiments typically used 5-10 mg of sample in dissolved in ~1.0–1.5 mL of CH_2Cl_2 . The compounds *trans*-[W(N₂)₂(dppe)(P^{Et}N^{Me}P^{Et})],¹⁵ [4-BrPhNH₃][OTf],³⁷ and [Et₃NH][BPh₄]³⁸ were synthesized by previously reported procedures. Elemental analysis was performed by Atlantic Microlabs, Norcross, GA

 $Et_2P(CH_2)_3PEt_2$ (depp). A 250 mL Schlenk flask was charged with 1.5 g (17 mmol) of diethylphosphine dissolved in 20 mL pentane followed by 10 mL of 1.6 M *n*-BuLi in hexanes. After 1 h, the solvent was removed under reduced pressure, affording a white solid. The solids were dissolved in 100 mL of THF and cooled to -78 °C before adding 0.84 mL (1.7 g, 8.3 mmol) of 1,3-dichloropropane. The reaction mixture was warmed to 21 °C and stirred for 90 min. The solvent was removed under reduced pressure, affording a cloudy oil. The oil was dissolved in 20 mL of pentane and filtered through Celite, and the solvent was removed under reduced pressure, affording a clear oil. Yield: 89% (1.56 g, 7.08 mmol). The ¹H and ³¹P NMR spectral data of the product matched previously reported values.³⁹ *trans*-[W(N₂)₂(H)(dppe)(P^{Et}N^{Me}P^{Et})][BF₄] ([3(N₂)₂]BF₄). Neat

HBF₄·Et₂O (3.3 μ L, 2.4 × 10⁻² mmol) was injected into a yellow CD_2Cl_2 solution of trans-[W(N_2)_2(dppe)(P^{Et}N^{Me}P^{Et})] (1(N₂)₂; 6.6 mg, 7.6×10^{-3} mmol) at -78 °C, resulting in a pale yellow solution. The NMR tube was mixed by inversion before promptly being inserted into an NMR probe, maintained at -35 °C. The products described below are formed depending on the temperature of the reaction mixture during mixing. ¹H NMR (CD_2Cl_2 , -35 °C): δ 7.64– 7.35 (m, 20H, PPh₂), 2.94 (s, 2H, PCH₂N), 2.85 (s, 2H, PCH₂N), 2.56-2.35 (m, 4H, PCH2CH2P), 2.33 (s, 3H, NCH3), 1.90 (m, 4H, PCH₂CH₃), 1.47 and 1.36 (m, 4H, PCH₂CH₃), 0.93 (dt, 6H, J_d = 15.3 Hz, $J_t = 7.3$ Hz, PCH₂CH₃), 0.77 (dt, 6H, $J_t = 14.0$ Hz, $J_t = 7.3$ Hz, PCH_2CH_3), -3.76 (dddd, 1H, $J_{HP} = 77.0 \text{ Hz}$, $J_{HP} = 77.0 \text{ Hz}$, $J_{HP} = 11.2$ Hz, $J_{HP} = 11.2$ Hz, W-H). ${}^{31}P{}^{1}H}$ NMR (CD₂Cl₂, -35 °C): δ 61.0 (dd with ¹⁸³W satellites $J_{PW} = 196$ Hz, 1P, $J_{PP} = 44$, 33, and 17 Hz, dppe), 34.7 (ddd with ¹⁸³W satellites $J_{PW} = 230$ Hz, 1P, $J_{PP} = 49$, 33, and 33 Hz, dppe), -15.5 (ddd with ¹⁸³W satellites $J_{PW} = 170$ Hz, 1P, $J_{PP} = 58$, 49, and 17 Hz, $P^{Et}N^{Me}P^{Et}$), -29.2 (ddd with ¹⁸³W satellites T^{PW} satellites $J_{\rm PW}$ = 208 Hz, 1P, $J_{\rm PP}$ = 58, 44, and 33 Hz, $P^{\rm Et}N^{\rm Me}P^{\rm Et}$). ¹⁵N NMR $(CD_2Cl_2, -35 \text{ °C}): \delta - 362$ (t, 1N, $J_{NP} = 14$ Hz, NMe). IR $(CH_2Cl_2, -35 \text{ °C}): \delta - 362$ (t, 1N, $J_{NP} = 14$ Hz, NMe). -41 °C, $\nu_{\rm NN}$, cm⁻¹): 1995 (s, asym). This protonated product is thermally sensitive and does not persist at ambient temperature.

trans-[W(N₂)₂(H)(dppe)(P^{Et}N^{Me}(H)P^{Et})][BF₄]₂ ([3(N₂)₂(NH)]-[BF₄]₂). ¹H NMR (CD₂Cl₂, -35 °C): δ 7.7 (br, N(H)Me, from ¹H-¹⁵N HSQC data with ¹⁵N-amine), -4.33 (ddd, 1H, J_{HP} = 87.4 Hz, J_{HP} = 75.4 Hz, J_{HP} = 12.1 Hz, J_{HP} = 8.9 Hz, W-H). ³¹P{¹H} NMR (CD₂Cl₂, -35 °C): δ 59.8 (ddd with ¹⁸³W satellites J_{PW} = 198 Hz, 1P, J_{PP} = 32, 21, and 47 Hz, dppe), 36.3 (ddd with ¹⁸³W satellites J_{PW} = 228 Hz, 1P, J_{PP} = 32, 47, and 32 Hz, dppe), -2.6 (ddd with ¹⁸³W satellites J_{PW} = 277 Hz, 1P, J_{PP} = 21, 47, and 59 Hz, P^{Et}N^{Me}P^{Et}), -16.3 (ddd with ¹⁸³W satellites J_{PW} = 222 Hz, 1P, J_{PP} = 47, 32, and 59 Hz, P^{Et}N^{Me}P^{Et}). ¹⁵N NMR (CD₂Cl₂, -35 °C, for ¹⁵N₂ labeled versions): δ -80 (s, 1N, W-N≡N), -43 (s, 1N, W-N≡N), -341 (d, 1N, J_{NH} = 79 Hz, N(H)Me). IR (CH₂Cl₂, -40 °C, ν_{NN}, cm⁻¹): 2017 (s, asym). This protonated product is thermally sensitive and does not persist at ambient temperature.

[W(NNH₂)(F)(dppe)(P^{Et}N^{Me}(H)P^{Et})][BF₄]₂ ([1(NNH₂)(F)(NH)]-[BF₄]₂). Following the procedure above for the synthesis of *trans*. [W(N₂)₂(H)(dppe)(P^{Et}N^{Me}(H)P^{Et})][BF₄]₂ from HBF₄:Et₂O, ~15% of the product formed is [W(NNH₂)(F)(dppe)(P^{Et}N^{Me}(H)P^{Et})]-[BF₄]₂. ¹H NMR (CD₂Cl₂, -35 °C): δ 10.55 and 10.33 (br, N(H)Me, from ¹H-¹⁵N HSQC data with ¹⁵N-amine), 5.63 (bs, NNH₂). ³¹P{¹H} NMR (CD₂Cl₂, -35 °C): δ 35.4 (dd, 1P, J_{PP} = 144 Hz, J_{PF} = 48 Hz), 10.8 (dd, 1P, J_{PP} = 144 Hz, J_{PF} = 44 Hz). ¹⁹F NMR (CD₂Cl₂, -35 °C): δ -187 (m). This protonated product is thermally sensitive and does not persist at ambient temperature.

[W($^{15}N^{15}NH_2$)(F)(dppe)(P^{Et}N^{Me}(H)P^{Et})][BF₄]₂ ([1($^{15}N^{15}NH_2$)(F)-(NH)][BF₄]₂). ¹H NMR (CD₂Cl₂, -35 °C): δ 5.63 (d, J_{HN} = 80 Hz, NNH₂). ¹⁵N{¹H} NMR (CD₂Cl₂): δ -80.0 (s, 1N, W-NNH₂), -45.7 (s, 1N, W-NNH₂).

Neat HOTf $(3.4 \,\mu L, 3.9 \times 10^{-2} \text{ mmol})$ was injected into a ca. 1 mL CD₂Cl₂ solution of *trans*-[W(¹⁵N₂)₂(dppe)(P^{Et}N^{Me}P^{Et})] (5.5 mg, 6.3 \times 10⁻³ mmol) at -78 °C, resulting in a pale yellow solution. After the entire length of the NMR tube was cooled, the contents were mixed by inversion before promptly inserting into a -40 °C NMR probe. A mixture of products was observed, including W hydrazido, a seven-coordinate W hydride with a protonated pendant amine, and a minor product that is unassigned.

trans-[W(¹⁵N₂)₂(H)(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf]₂ ([3(¹⁵N₂)₂(NH)]-[OTf]₂). ¹H NMR (CD₂Cl₂, -40 °C): δ -4.32 (ddd, 1H, *J*_{HP} = 85, 76, 12, 12 Hz, W-H); due to multiple overlapping ¹H resonances for the mixture of [3(¹⁵N₂)₂(NH)][OTf]₂ and [1(¹⁵N¹⁵NH₂)(OTf)-(NH)][OTf]₂, the resonances in the aliphatic region of the ¹H NMR spectrum were difficult to assign. ³¹P{¹H} NMR (CD₂Cl₂, -40 °C): δ 63.7 (ddd, 1P, *J*_{PP} = 47, 32, and 20 Hz, dppe), 43.6 (ddd, 1P, *J*_{PP} = 70, 31, and 31 Hz, unassigned), 40.1 (ddd, 1P, *J*_{PP} = 47, 32, and 31 Hz, dppe), 8.1 (ddd, 1P, $J_{\rm PP} = 70$, 57, and 12 Hz, unassigned), 0.2 (ddd, 1P, $J_{\rm PP} = 59$, 47, and 20 Hz, $P^{\rm Et}N^{\rm Me}({\rm H})P^{\rm Et}$), -13.6 (ddd, 1P, $J_{\rm PP} = 59$, 47, and 31 Hz, $P^{\rm Et}N^{\rm Me}({\rm H})P^{\rm Et}$). ¹⁵N{¹H} NMR (CD₂Cl₂, -40 °C): δ -44 (s, W-N \equiv N), -81 (s, W-N \equiv N). This protonated product is thermally sensitive and does not persist at ambient temperature.

 $trans - [W(N_2)_2(H)(dppe)(P^{Et}(^{15}N)^{Me}(H)P^{Et}][OTf]_2$ ([3(¹⁵N_2)_2(¹⁵NH)][OTf]_2). ¹⁵N{¹H} NMR (CD_2Cl_2, -40 °C): δ -341 (s). ¹H-coupled ¹⁵N NMR (CD_2Cl_2, -40 °C): δ -341 (d, J_{NH} = 78 Hz).

trans-[W(¹⁵N¹⁵NH₂)(OTf)(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf]₂ ([1(¹⁵N¹⁵NH₂)(OTf)(NH))[OTf]₂). ¹H NMR (CD₂Cl₂, -40 °C): δ 6.54 (d, $J_{\text{HN}} = 89$ Hz, ¹⁵N¹⁵NH₂). ³¹P{¹H} NMR (CD₂Cl₂, -40 °C): δ 35.4 (m, $J_{\text{PP}} = 127$, dppe), 2.7 (m, $J_{\text{PP}} = 127$ Hz, PNP). ¹⁵N{¹H} NMR (CD₂Cl₂, -40 °C): δ -47 (s, W–NNH₂), -80 (s, 1N, W-NNH₂). This protonated product is thermally sensitive and does not persist at ambient temperature.

trans-[W(¹⁵N₂)₂(H)(dppe)(P^{Et}N^{Me}P^{Et})][OTf] ([3(¹⁵N₂)₂][OTf]). ¹H NMR (CD₂Cl₂, -30 °C): δ 7.63–7.22 (m, 20H, PPh₂), 2.94 (s, 2H, PCH₂N), 2.84 (s, 2H, PCH₂N), 2.56–2.32 (m, 4H, PCH₂CH₂P), 2.34 (s, 3H, NCH₃), 1.90 (m, 4H, PCH₂N), 1.54–1.30 (m, 4H, PCH₂N), 0.93 (dt, 6H, J_d = 15.2 Hz, J_t = 7.3 Hz, CH₂CH₃), 0.77 (dt, 6H, J_d = 13.8, Hz, J_t = 7.3 Hz, CH₂CH₃), -3.77 (tt, 1H, J_t = 77.3 Hz, J_t = 11.0 Hz, W–H). ³¹P{¹H} NMR (CD₂Cl₂, -30 °C): δ 61.0 (ddd with ¹⁸³W satellites J_{PW} = 183 Hz, 1P, J_{PP} = 45, 33, and 17 Hz, dppe), 34.7 (ddd with ¹⁸³W satellites J_{PW} = 231 Hz, 1P, J_{PP} = 49, 33, and 33 Hz, dppe), -15.6 (ddd with ¹⁸³W satellites J_{PW} = 170 Hz, 1P, J_{PP} = 59, 49, and 17 Hz, P^{Et}N^{Me}P), -29.3 (ddd with ¹⁸³W satellites J_{PW} = 215 Hz, 1P, J_{PP} = 59, 45, and 33 Hz, P^{Et}N^{Me}P). ¹⁵N{¹H} NMR (CD₂Cl₂, -30 °C): δ -47.3 (d, J_{NN} = 4 Hz, 1N, W–N≡N), -75.4 (d, J_{NN} = 2 Hz with J_{NW} = 49 Hz ¹⁸³W satellites, 1N, W-N≡N). This protonated product is thermally sensitive and does not persist at ambient temperature.

trans-[W(N₂)₂(dppe)(depp)] (2(N₂)₂). To a 100 mL roundbottom flask with a large stir bar were placed $W(\textrm{dppe})\textrm{Cl}_4$ (0.320 g, 0.442 mmol), depp (0.102 g, 0.464 mmol), magnesium powder (1.0 g), and 50 mL of THF, and the mixture was stirred vigorously for 72 h under an atmosphere of N2. The solution was filtered to remove Mg solids and the solvent removed under reduced pressure. The product was extracted with pentane (8 \times 60 mL). The remaining orangebrown solid (crude yield 0.26 g) was stirred in pentane (1 L) and filtered, leaving behind a tan solid. The pentane was removed under reduced pressure, affording a bright orange solid. This material was recrystallized from a pentane/THF solution (10/1) at -20 °C and dried under vacuum, resulting in a bright orange solid (31 mg, 8%). ¹H NMR (CD₂Cl₂): δ 7.47-7.25 (m, 20H, P(C₆H₅)), 2.14 (m, 4H, Ph₂PCH₂), 1.94 (m, 4H, Et₂P(CH₂)CH₂), 1.85 (m, 2H, Et₂P(CH₂)-CH₂), 1.83 (m, 4H, PCH₂CH₃), 1.63 (m, 4H, PCH₂CH₃), 0.69 (dt, 12H, PCH₂CH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ 44.6 (s (br), 2P, dppe), -16.8 (s (br), 2P, depp). ${}^{31}P{}^{1}H$ NMR (THF- d_8): δ 43.9 (m, 2P, dppe), -16.3 (m, 2P, depp). IR (KBr, ν_{NN} (cm⁻¹)): 1919 (s, asym), 1981 (w, asym). Anal. Calcd for C₃₇H₅₀N₄P₄W: C, 51.76; H, 5.87; N, 6.53. Found: C, 51.63; H, 5.78; N, 6.49.

[W(NNH₂)(OTf)(dppe)(depp)][OTf] ([2(NNH₂)(OTf)][OTf]). In a septum-capped NMR tube, 6.2 mg (7.2 \times 10^{-3} mmol) trans- $[W(N_2)_2(dppe)(depp)]$ was dissolved in 1 mL of CD_2Cl_2 cooled to -78 °C, and treated with 2.0 μ L (2.2 × 10⁻² mmol) of HOTf. The contents were mixed, and the tube was returned to the cold bath for an additional 10 min before inserting the sample into an NMR spectrometer that was precooled to -40 °C. NMR spectral data collected at -40 °C are consistent with the formation of $[2(NNH_2)-$ (OTf)][OTf]; however, the ¹H NMR resonances were broad at this temperature. ¹H NMR (CD₂Cl₂, 22 °C): δ 8.94 (bs, NNH₂), 7.52-7.38 (m, 20H, PPh₂), 2.80 (m, 4H, Ph₂PCH₂CH₂Ph₂), 2.44 and 2.25 (m, 4H, $Et_2PCH_2CH_2CH_2PEt_2$), 2.43 and 1.85 (m, 2H, Et₂PCH₂CH₂CH₂PEt₂), 2.00, 1.72, 1.85, 1.71 (m, 8H, CH₃CH₂P), 0.90 (m, 12H, CH₃CH₂P). ³¹P{¹H} NMR (CD₂Cl₂, 22 °C): δ 31.5 (m, 2P, dppe), -14.1 (m, 2P, depp). ¹⁹F NMR (CD₂Cl₂, 22 °C): δ -76 (s, W-OTf). ¹³C{¹H} NMR (CD₂Cl₂, 22 °C): δ 133.4–128.9 (C₆H₅P of dppe), 31.4 (PhPCH₂ of dppe), 23.5 (CH₃CH₂P of depp), 23.4 (CH₃CH₂P of depp), 20.4 (EtPCH₂CH₂CH₂ of depp), 19.8 (CH₃CH₂P of depp), 18.4 (EtPCH₂CH₂CH₂ of depp), 8.8 (CH₃CH₂P of depp).

[W(NND₂)(OTf)(dppe)(depp)][OTf]. This compound was prepared by the same method as above with DOTf. IR (KBr, 21 °C, NND₂): 2506 (w, N-D), 2386 (w, N-D), 2325 (w) cm⁻¹.

[W(NNH₂)(F)(dppe)(depp)][BF₄] ([2(NNH₂)(F)][BF₄]). Neat HBF₄·Et₂O (1.5 μL, 1.1 × 10⁻² mmol) was injected into a CD₂Cl₂ solution of *trans*-[W(N₂)₂(dppe)(depp)] (2.8 mg, 3.3 × 10⁻³ mmol) at -78 °C. The NMR tube was mixed by inversion before promptly being inserted into a NMR probe maintained at -40 °C. ¹H NMR (CD₂Cl₂, -40 °C): δ 5.24 (bs, NNH₂). ³¹P[¹H} NMR (CD₂Cl₂, -40 °C): δ 36.7 (dd, 2P, J_{PP} = 143 Hz, J_{PF} = 49 Hz), -2.1 (dd, 2P, J_{PP} = 143 Hz, J_{PF} = 41 Hz). ¹⁹F NMR (CD₂Cl₂, -40 °C): δ -150 (bs, BF₄⁻) -185 (tt, J_{FP} = 41 Hz, J_{FP} = 49 Hz, W-F). *cis*-[W(¹³CO)₂(dppe)(P^{Et}N^{Me}P^{Et})] (*cis*-[1(¹³CO)₂]). A Teflon-

cis-[W(¹³CO)₂(dppe)(P^{Et}N^{Me}P^{Et})] *(cis*-[1(¹³CO)₂]). A Teflonvalved NMR tube was loaded with *trans*-[W(N₂)₂(dppe)(P^{Et}N^{Me}P^{Et})] (9.0 mg, 0.010 mmol) dissolved in ca. 1 mL THF-*d*₈, affording an orange solution. The tube was degassed and charged with 1 atm of ¹³CO and mixed by repeated inversion for 37 h, resulting in >98% conversion to the desired product¹⁵ as a yellow solution (see the Supporting Information). ¹³C{¹H} NMR (THF-*d*₈, 21 °C): δ (¹³CO) 221.0 (ddddd with ¹⁸³W satellites *J*_{PW} = 154 Hz, 1C, *J*_{CP} = 21.0, 9.5, 6.0, 5.4 Hz, *J*_{CC} = 4.2 Hz), 218.7 (ddddd with ¹⁸³W satellites *J*_{PW} = 146 Hz, 1C, *J*_{CP} = 28.0, 8.0, 8.0, 5.5 Hz, *J*_{CC} = 4.2 Hz). ³¹P{¹H} NMR (THF-*d*₈, 21 °C): δ 46.8 (ddddd with ¹⁸³W satellites *J*_{PW} = 281 Hz, 1P, *J*_{PP} = 74.3, 18.5, 8.7 Hz, *J*_{PC} = 8.0, 5.4 Hz), 39.8 (ddddd with ¹⁸³W satellites *J*_{PW} = 219 Hz, 1P, *J*_{PP} = 18.5, 18.5, 8.7 Hz, *J*_{PC} = 28.0, 6.0 Hz), -11.2 (ddddd with ¹⁸³W satellites *J*_{PW} = 274 Hz, 1P, *J*_{PP} = 74.3, 27.9, 18.5 Hz, *J*_{PC} = 9.5, 5.5 Hz), -25.5 (ddddd with ¹⁸³W satellites *J*_{PW} = 202 Hz, 1P, *J*_{PP} = 27.9, 18.5, 18.5 Hz, *J*_{PC} = 21.0, 8.0 Hz). IR (KBr, ν_{CO}, cm⁻¹): 1792 (s, sym), 1729 (s, asym).

trans-[W(¹³CO)₂(dppe)(P^{Et}N^{Me}P^{Et})] (*trans*-[1(¹³CO)₂]). ¹³C{¹H} NMR (THF- d_{s} , 21 °C): δ (¹³CO) 213.2 (bm with ¹⁸³W satellites J_{PW} = 123 Hz, ³¹P{¹H} NMR (THF- d_{s} , 21 °C): δ 53.6 (m with ¹⁸³W satellites J_{PW} = 287 Hz, 2P), -10.6 (m with ¹⁸³W satellites J_{PW} = 315 Hz, 2P). IR (KBr, ν_{CO} , cm⁻¹): 1785 (s, asym).

trans-[W(CO)₂(H)(dppe)(P^{Et}N^{Me}(H)P^{Et})][OTf]₂ ([3(CO)₂(NH)]-[OTf]₂). *p*-Bromoanilinium triflate (10.3 mg, 0.0320 mmol) was added to the above solution of *cis*-[W(CO)₂(dppe)(P^{Et}N^{Me}P^{Et})] at 21 °C and agitated, affording a pale yellow solution. ³¹P{¹H} NMR (THF-*d*₈, 21 °C): δ 60.7 (bm, 1P, *J* = 27 Hz), 43.6 (m with ¹⁸³W satellites *J*_{PW} = 201 Hz, 1P, *J* = 30 Hz), -11.6 (bs, 1P), -23.4 (bs, 1P). ¹H NMR (THF-*d*₈, 21 °C): δ 7.74-6.95 (m, 20H, PPh₂), 2.96 (s, 2H, PCH₂N), 2.94 (s, 2H, PCH₂N), 2.67-2.54 (m, 2H, PCH₂CH₂P), 2.33-2.20 (m, 2H, PCH₂CH₂P), 2.37 (s, 3H, NCH₃), 2.06-1.95 (m, 4H, PCH₂CH₃), 1.44-1.33 (m, 4H, PCH₂CH₃), 0.93 (dt, 6H, *J*_{HP} = 15.7 Hz, *J*_t = 7.2 Hz, PCH₂CH₃), 0.76 (dt, 6H, *J*_{HP} = 14.4 Hz, *J*_t = 7.2 Hz, PCH₂CH₃), -5.18 (dddd, 1H, *J*_t = 78.0 Hz, *J*_t = 13.8 Hz, W-H). IR (KBr, ν_{CO}, cm⁻¹): 1957 (w, sym), 1851 (s, asym). *trans*-[W(CO)₂(H)(dppe)(P^{Et}(¹⁵N)(H)^{Me}P^{Et})][OTf]₂. ¹⁵N{¹H}

trans-[W(CO)₂(H)(dppe)($P^{\text{ft}}(^{15}\text{N})(\text{H})^{\text{Me}}P^{\text{ft}})$][OTf]₂. ¹⁵N{¹H} NMR (THF-*d*₈, 21 °C): δ -338 (s, ¹⁵NC*H*₃). Proton-coupled ¹⁵N NMR (THF-*d*₈, 21 °C): δ -338 (d, *J*_{NH} = 76 Hz, ¹⁵NC*H*₃).

Regeneration of *cis*-[W(CO)₂(dppe)(P^{Et}N^{Me}P^{Et})] with Et₃N. The above solution containing $[3(CO)_2(NH)][OTf]_2$ was degassed and placed under an atmosphere of ¹⁵N₂ in a septum-capped NMR tube. Triethylamine (14 μ L, 0.10 mmol) was injected into the NMR tube at room temperature, resulting in immediate darkening of the yellow color (see the Supporting Information). The NMR spectra match those of *cis*-[W(CO)₂(dppe)(P^{Et}N^{Me}P^{Et})].

Protonolysis Procedure and Quantification of Ammonium. A known amount of complex $1(N_2)_2$ or $2(N_2)_2$ was dissolved in 10 mL of dichloromethane, resuling in a orange solution. While the solution was stirred, triflic acid (100 equiv) was added, resulting in a pale orange solution for $1(N_2)_2$ and a light green solution for $2(N_2)_2$. After the mixture was stirred vigorously for 20 h, it was frozen with liquid nitrogen and a solution of KO^tBu (200 equiv) in THF/MeOH (2 mL/8 mL) was added. The solution was stirred vigorously while it was warmed to room temperature. The volatiles were distilled under vacuum into a flask submerged in liquid nitrogen which contained 4 mL of a 2 M aqueous HCl solution. The reaction mixtures were analyzed for NH₃ and N₂H₄ using the indophenol method⁴⁰ and *p*-(dimethylamino)benzaldehyde reagent,⁴¹ respectively. Table S1 in the Supporting Information contains the compiled results of NH₃ quantification. The following elemental analysis results were obtained for the microcrystalline solid of $1(N_2)_2$ used in the protonolysis reactions for NH₃ production: Anal. Calcd for C₃₇H₅₁N₅P₄W: C, 50.87; H, 5.88; N, 8.02. Found: C, 50.63; H, 5.98; N, 8.19.

For the ¹H NMR experiments comparing the formation of NH₄⁺ and ¹⁵NH₄⁺ from $1(N_2)_2$ and $1(^{15}N_2)_2$, respectively, triflic acid (50 μ L, 5.7 × 10⁻⁴ mol) was added to a 1.0 mL solution of 5.5 × 10⁻⁶ mol of the tungsten dinitrogen complex dissolved in CH₂Cl₂ and the mixture was stirred for 18 h at 21 °C. The solvent was removed under vacuum, and the solids were dissolved in DMSO- d_6 ,⁴²

Theoretical Calculations. All structures were fully optimized without symmetry constraints using the B3P86⁴³ functional as impletemented in Gaussian 09.⁴⁴ The Stuttgart basis set with effective core potential (ECP)⁴⁵ was used for the W atom and the 6-31G* basis set⁴⁶ was used for other nonmetal atoms, with the exception that for hydrogen atoms bound directly to nitrogen atoms, a polarization function was added. Each stationary point was confirmed by frequency calculations at the same level of theory to be areal minimum without imaginary frequency. The gas-phase free energy was corrected with ZPE, thermal corrections, and entropy terms at the state of 1 atm and 298 K. The solvation free energy contribution to total free energy in THF was calculated by using the C-PCM model⁴⁷ in Gaussian 09 at the same level of theory as that for optimization. Bondi radii were used with a scale factor (α) of 1.0. All calculated pK_a values and proton affinities (1.364 × pK_a) are for THF solutions and are calculated relative to the value of Et₃NH⁺ ($pK_a = 12.5$),⁴⁸ which is assigned as an experimental value to anchor the calculated pK_a scale.

X-ray Diffraction Study. X-ray diffraction data were collected on a Bruker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo K α radiation. A selected crystal was mounted using Paratone oil onto a cryoloop and cooled to the data collection temperature of 140 K. Unit cell parameters were obtained from 36 data frames, 0.5° Φ , from three different sections of the Ewald sphere. Cell parameters were retrieved using APEX II software⁴⁹ and refined using SAINT+⁵⁰ on all observed reflections. Each data set was treated with SADABS⁵¹ absorption corrections on the basis of redundant multiscan data. The structure was solved with the Olex2 structure solution program using charge flipping and refined by least-squares methods on F^2 using the SHELXL program package⁵² in the Olex2 structure solution program.⁵³

ASSOCIATED CONTENT

S Supporting Information

Figures, tables, and a CIF file giving NMR and IR spectral data, crystallographic information, and Cartesian coordinates for computed molecules. 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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