

# Synthesis and Photodriven Hydrogenation of Tungsten Nitride Complexes Prepared from Dinitrogen Cleavage

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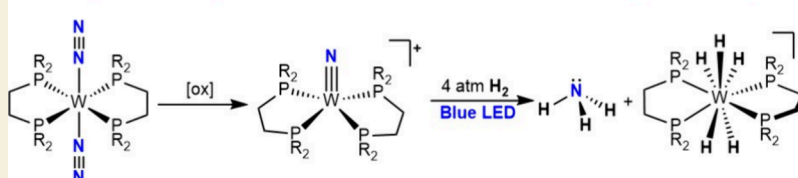


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Supporting Information

## Dinitrogen Cleavage and Ammonia Generation with a Tungsten Complex



**ABSTRACT:** Oxidation of the Chatt-type tungsten dinitrogen compound, *trans*-(depe)<sub>2</sub>W(N<sub>2</sub>)<sub>2</sub> (depe = Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>), with [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe][BARF<sub>4</sub>] (BARF<sub>4</sub> = B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>) resulted in isolation of [(depe)<sub>2</sub>WN][BARF<sub>4</sub>], a rare example of a tungsten(IV) nitride prepared from N<sub>2</sub> cleavage. A bimetallic μ-N<sub>2</sub> ditungsten intermediate supported by terminal N<sub>2</sub> ligands was identified, and irradiation with visible light promoted dinitrogen cleavage and formation of [(depe)<sub>2</sub>WN][BARF<sub>4</sub>]. Performing the analogous one-electron oxidation of the related tungsten dinitrogen compound, *trans*-(dppe)<sub>2</sub>W(N<sub>2</sub>)<sub>2</sub> (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), furnished the corresponding cationic, 17-electron tungsten dinitrogen complex, [(dppe)<sub>2</sub>W(N<sub>2</sub>)<sub>2</sub>][BARF<sub>4</sub>], that was characterized by X-ray diffraction and vibrational and EPR spectroscopies. The generation of [(dppe)<sub>2</sub>W(N)][BARF<sub>4</sub>] was observed in low yield from the *in situ* formed mixed N<sub>2</sub>-bridged compound, [(N<sub>2</sub>)<sub>2</sub>(depe)<sub>2</sub>W(μ-N<sub>2</sub>)W(dppe)<sub>2</sub>(N<sub>2</sub>)][BARF<sub>4</sub>]<sub>2</sub>, and was confirmed by independent synthesis using 1-azidoadamantane. Addition of ammonia or water to [(depe)<sub>2</sub>WN][BARF<sub>4</sub>] resulted in formation of the cationic imide and hydroxide complexes, [(depe)<sub>2</sub>W(NH)(X)][BARF<sub>4</sub>] (X = NH<sub>2</sub>, OH). Irradiation of [(depe)<sub>2</sub>WN][BARF<sub>4</sub>] with 440 nm visible light in the presence of Ir(ppy)<sub>3</sub> (ppy = 2-phenylpyridine) under 4 atm of dihydrogen resulted in hydrogenation of the tungsten nitride to the cationic tungsten pentahydride, [(depe)<sub>2</sub>WH<sub>5</sub>][BARF<sub>4</sub>], with the release of free ammonia in 21% yield, a rare example of ammonia generation from dinitrogen and dihydrogen from a well-defined tungsten nitride.

**KEYWORDS:** tungsten, dinitrogen cleavage, terminal nitride, hydrogenation, mechanism

## INTRODUCTION

The synthesis of ammonia from its elements with molecular compounds is a long-standing challenge in synthetic chemistry. While the industrial Haber–Bosch process has enabled the widespread distribution of ammonia-based fertilizers for over a century,<sup>1</sup> replicating N<sub>2</sub> hydrogenation with molecular compounds may provide fundamental insights into N–H bond formation and enable more energy efficient and carbon-neutral reactions. Although N<sub>2</sub> coordination and cleavage by organometallic and coordination compounds is well preceded,<sup>2–4</sup> subsequent N–H bond formation from the resulting metal nitrides has proven challenging, especially when using H<sub>2</sub> as the hydrogen atom source.<sup>5–9</sup> The formation of strong M≡N bonds after dinitrogen cleavage consequently results in low N–H bond dissociation free energies, often below the threshold for spontaneous formation of dihydrogen.<sup>10</sup> Alternative strategies, such as the hydrogenation of activated side-on metal dinitrogen compounds<sup>11</sup> and proto-

nation from coordinated dihydrogen,<sup>12</sup> have been used for N–H bond formation and ammonia synthesis. One notable example was reported by Hidai and co-workers, where a ruthenium η<sup>2</sup>-dihydrogen complex was used to protonate a Chatt-type tungsten dinitrogen compound, resulting in 55% yield of free ammonia (Scheme 1a, left).<sup>13</sup>

Our laboratory has demonstrated the application of visible light in promoting N–H bond formation from terminal metal nitrides. Initial studies demonstrated that ruthenium photocatalysts in combination with dihydroacridine were effective for the hydrogenation of terminal manganese nitrides to

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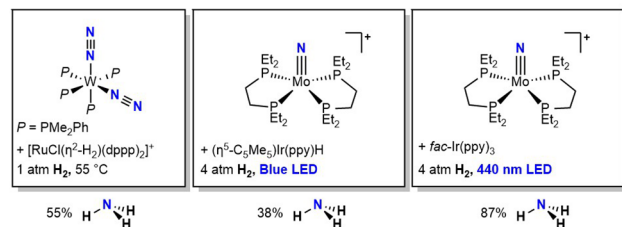
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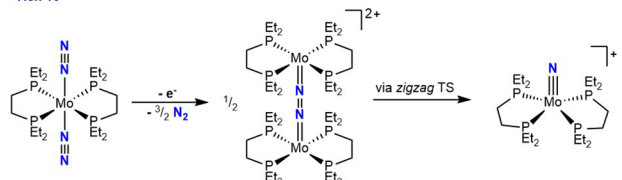
## Scheme 1. Dinitrogen Hydrogenation and Cleavage by Homogeneous Group 6 Metal Compounds

### A. Reported Hydrogenations of Group 6 Compounds to Yield Ammonia from $N_2$ and $H_2$



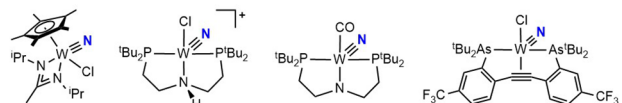
### B. One-Electron Oxidation Induced $N_2$ Cleavage

Ref. 19



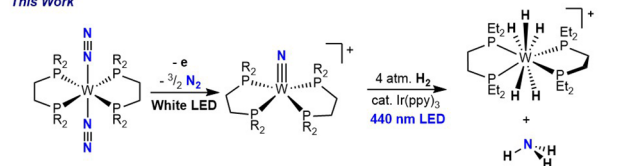
### C. Previous Examples of $N_2$ -Derived Terminal Tungsten Nitrides

Refs. 21–24



### D. One-Electron Oxidation Induced Cleavage of $N_2$ on Tungsten Bisphosphines and W(IV) Nitride Reactivity Towards Hydrogenation

This Work



produce up to 80% yield of free ammonia.<sup>14</sup> A subsequent report established that blue-light irradiation of dihydroacridine in the absence of a metal photocatalyst was also effective for ammonia synthesis from manganese nitrides with ammonia yields of up to 85% under optimized conditions.<sup>15</sup>

Ammonia synthesis was also demonstrated in the photo-driven hydrogenation of the  $N_2$ -derived molybdenum nitride,  $[(depe)_2MoN][BAR^F_4]$ , in the presence of the piano-stool iridium hydride,  $(\eta^5-C_5Me_5)Ir(ppy)H$  (Scheme 1a, middle).<sup>8</sup> Use of  $fac-Ir(ppy)_3$  as the photocatalyst and additional reaction optimization resulted in near quantitative yields of 87% of ammonia and enabled a synthetic cycle whereby the resulting cationic molybdenum pentahydride was used to promote  $N_2$  cleavage and regeneration of  $[(depe)_2MoN][BAR^F_4]$  (Scheme 1a, right). Ultimately, superstoichiometric ammonia generation in 112% yield was accomplished after three synthetic cycles.<sup>9</sup>

Phosphine-supported group 6 transition metal dinitrogen complexes were first studied by Chatt<sup>16</sup> and further investigated by Hidai.<sup>17</sup> These compounds exhibit weakly activated, end-on bound dinitrogen ligands that, in certain cases, yield ammonia when treated with strong acid.<sup>18</sup> In 2019, Masuda and co-workers reported that the addition of a one-electron ferrocenium oxidant to  $trans-(depe)_2Mo(N_2)_2$  promoted dinitrogen cleavage to furnish the corresponding molybdenum nitride,  $[(depe)_2MoN][BAR^F_4]$ , in 62% yield (Scheme 1b).<sup>19</sup> One-electron oxidation of the  $Mo(0)$ ,  $d^6$

complex formed a  $\mu-N_2$  bimetallic  $Mo(I)$  dinitrogen compound with 10  $\pi$ -electrons that achieves the geometric and electronic requirements to access the “zigzag” transition state and promote  $N_2$  cleavage.<sup>20</sup>

While dinitrogen cleavage with molybdenum compounds is well precedented,<sup>4</sup> analogous reactivity with tungsten remains rare (Scheme 1c). In 2015, Sita and co-workers reported the synthesis of a terminal nitride derived from dinitrogen on a tungsten center.<sup>21</sup> In this report, a tungsten nitride chloride supported by pentamethylcyclopentadiene and ethanimidamide ligands was accessed after the addition of trimethylsilyl chloride to a side-on bound bridging dinitrogen compound. In 2019, Schneider and co-workers described that the protonation of a MACHO-type ligand in a chloro tungsten bridging dinitrogen compound triggered the splitting of dinitrogen and yielded the terminal nitride under certain conditions.<sup>22</sup> Both the photodriven and the reversible thermal cleavage of  $N_2$  were observed in a related tungsten carbonyl derivative.<sup>23</sup> Most recently, Ballmann and Eberle have reported the cleavage of dinitrogen from a tungsten complex bearing a 2,2'-( $tBu_2As$ )<sub>2</sub>-substituted diphenylacetylene chelate.<sup>24</sup>

Reports of the hydrogenation of molecular  $N_2$ -derived transition metal nitrides with  $H_2$  as the terminal reductant to yield ammonia are uncommon in the literature,<sup>5–9</sup> with no reports of isolated tungsten nitride compounds exhibiting such reactivity. Recent reports have described catalytic ammonia formation from  $N_2$ -derived tungsten compounds using  $SmI_2/H_2O$ <sup>25</sup> as well as electrochemical methods that rely on proton-coupled electron transfer (PCET) mediators.<sup>26</sup> In addition to providing fundamental insights into dinitrogen cleavage, the synthesis of a tungsten congener of an  $N_2$ -derived molybdenum nitride is of interest to determine the limits of the photodriven hydrogenation strategy for strong metal–ligand multiple bonds. Tungsten nitride bonds are anticipated to be stronger than their molybdenum counterparts due to the established trends in bond strengths among transition metals.<sup>27</sup>

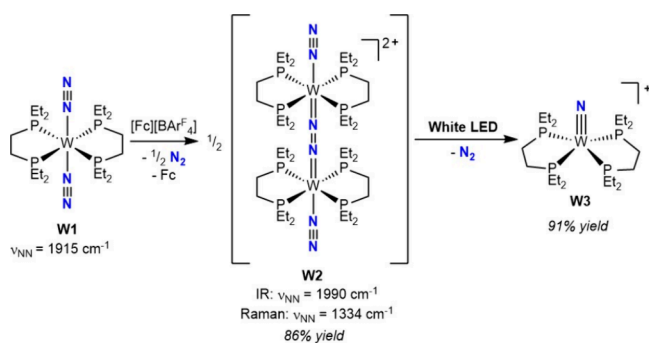
Here, we describe a rare example of dinitrogen cleavage from a Chatt-type tungsten dinitrogen complex by one-electron oxidation. An intermediate ditungsten complex with one bridging and two terminal dinitrogen ligands was observed that required photolysis to promote  $N_2$  scission and formation of the terminal tungsten nitride,  $[(depe)_2WN][BAR^F_4]$ . This metal nitride undergoes photodriven hydrogenation to yield ammonia and a cationic pentahydride in the presence of the photocatalyst  $Ir(ppy)_3$ , demonstrating the ability of this approach to cleave strong metal–ligand multiple bonds.

## RESULTS AND DISCUSSION

### Synthesis of a Tungsten(IV) Nitride by Oxidative Dinitrogen Cleavage

Our studies commenced with the synthesis and isolation of the Chatt-type tungsten dinitrogen compound,  $(depe)_2W(N_2)_2$  (**W1**).<sup>28</sup> Addition of  $[(\eta^5-C_5H_5)_2Fe][BAR^F_4]$  to a diethyl ether solution of **W1** resulted in formation of a yellow, paramagnetic, X-band EPR-silent tungsten product (Scheme 2). The diethyl ether solution infrared spectrum exhibited a strong band at  $1990\text{ cm}^{-1}$ , consistent with a terminal  $N_2$  stretch. As expected from oxidation, this band has a higher frequency than the value of  $1915\text{ cm}^{-1}$  for **W1**. The Raman spectrum recorded in diethyl ether solution exhibited an intense band centered at  $1334\text{ cm}^{-1}$ , assigned to the symmetric stretch of a bridging dinitrogen ligand.<sup>29</sup> This value is

### Scheme 2. One-Electron-Induced Cleavage of Dinitrogen by (depe)<sub>2</sub>W(N<sub>2</sub>)<sub>2</sub>



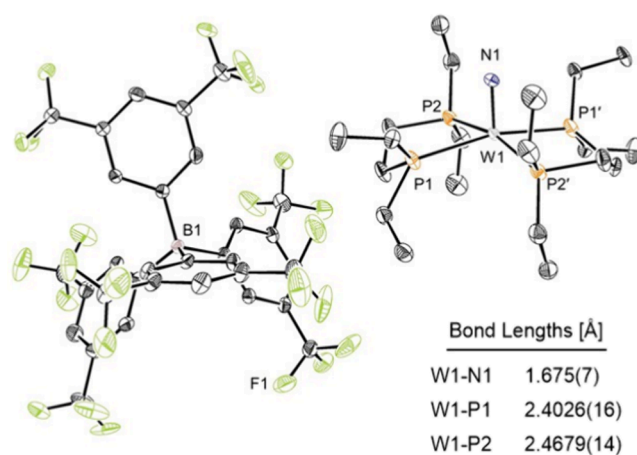
comparable to those previously reported for bridging group 6 transition metal dinitrogen complexes, including  $[(^t\text{BuPNP})\text{MoCl}]_2(\mu\text{-N}_2)$  ( $\nu_{\text{N}_2} = 1343 \text{ cm}^{-1}$ ,  $^t\text{BuPNP} = \text{N}(\text{CH}_2\text{CH}_2\text{P}^t\text{Bu}_2)_2$ )<sup>22</sup> and  $[(\text{depe})_2\text{Mo}]_2(\mu\text{-N}_2)$  ( $\nu_{\text{N}_2} = 1292 \text{ cm}^{-1}$ ).<sup>19</sup> Paramagnetic **W1** is NMR silent, and no change was observed upon cooling a THF-*d*<sub>8</sub> solution to  $-50^\circ\text{C}$ . Likewise, a THF-*d*<sub>8</sub> solution magnetic moment (Evans method) of  $2.0(6) \mu_{\text{B}}$  was measured at  $23^\circ\text{C}$ , lower than the spin-only value expected for two noninteracting  $d^1$  ions likely due to either spin interaction through the  $\mu\text{-N}_2$  ligand or spin-orbit coupling.

Based on the spectroscopic data, the product of the oxidation of **W1** was assigned as the dicationic, bimetallic tungsten(I) compound with one bridging and two terminal dinitrogen ligands,  $[(\text{depe})_2\text{W}(\text{N}_2)]_2(\mu\text{-N}_2)$  (**W2**, Scheme 2). This product is related to the intermediate proposed by Masuda and co-workers based on *in situ* resonance Raman experiments on the corresponding molybdenum derivative with the difference being the tungsten congener having terminal dinitrogen ligands.<sup>19</sup>

Although no change to THF or Et<sub>2</sub>O solutions of **W2** were observed upon heating to  $60^\circ\text{C}$  for 12 h, irradiation of a diethyl ether solution for 15 min with white LEDs either under dinitrogen or static vacuum led to complete conversion of the starting material. A color change from yellow to purple to dark red was observed, and the cationic tungsten nitride,  $[(\text{depe})_2\text{WN}][\text{BARF}_4]$  **W3**, was isolated in 91% yield (Scheme 2). It is likely that visible light promotes the dissociation of the terminal N<sub>2</sub> ligands to achieve the requisite coordination number and geometry to promote dinitrogen cleavage.<sup>20</sup> The distinction between photoinduced N<sub>2</sub> dissociation in tungsten complexes and thermal loss in corresponding molybdenum congeners has been previously reported in Chatt–Hidai-type group 6 complexes.<sup>30</sup> The <sup>31</sup>P NMR spectrum of **W3** in THF-*d*<sub>8</sub> exhibited a singlet at 67.9 ppm with <sup>183</sup>W satellites (<sup>1</sup>J<sub>PW</sub> = 151 Hz), similar to the value of 64.4 ppm reported by Masuda for the molybdenum congener.<sup>19</sup>

Vapor diffusion of pentane into a concentrated diethyl ether solution of **W3** at  $-35^\circ\text{C}$  produced dark-red crystals suitable for X-ray diffraction, and the solid-state structure confirmed the formation of **W3** (Figure 1). The W≡N bond length of 1.675(7) Å is comparable to the value of 1.646(6) Å reported for the molybdenum compound.<sup>19</sup> **W3** is a rare example of a crystallographically characterized W(IV) nitride<sup>23,24</sup> and is uniquely prepared by oxidative N<sub>2</sub> cleavage.

Extension of oxidative dinitrogen cleavage to another Chatt-type tungsten dinitrogen compound was also explored to determine the generality of the transformation. Treatment of



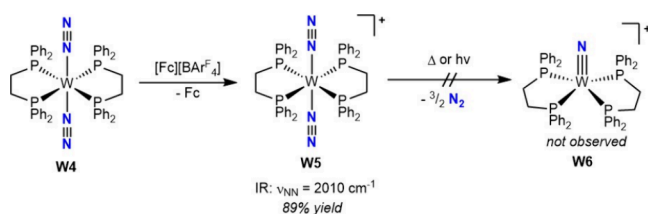
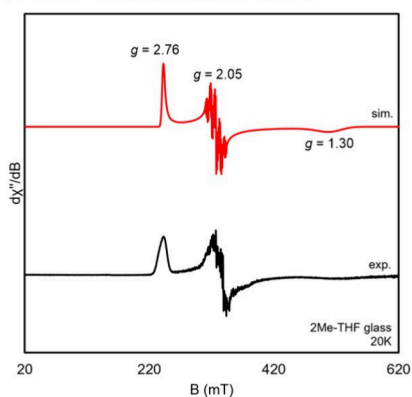
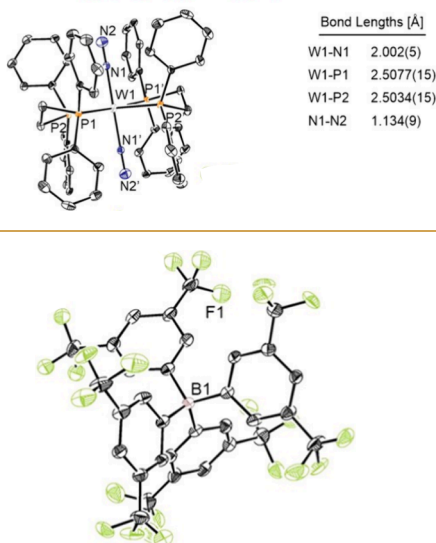
**Figure 1.** X-ray crystal structure of **W3**. Hydrogen atoms, equivalent moiety, and disorder omitted for clarity. Ellipsoids presented with 30% probabilities.

*trans*-(dppe)<sub>2</sub>W(N<sub>2</sub>)<sub>2</sub><sup>31</sup> (**W4**) with one equivalent of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{BARF}_4]$  resulted in rapid formation of a new paramagnetic tungsten product. The diethyl ether solution infrared spectrum ether contained a strong band at  $2010 \text{ cm}^{-1}$ , assigned as a terminal N<sub>2</sub> stretch. No bands assignable to bridging dinitrogen ligands were located in the corresponding diethyl ether solution Raman spectrum. Based on the vibrational data, the product of oxidation of **W4** was assigned as the cationic tungsten(I) bis(dinitrogen) compound **W5** (Scheme 3).

The spectroscopic data and structural assignment are consistent with a report by Colquhoun and Head,<sup>32</sup> where the synthesis of cationic *trans*- $[(\text{dppe})_2\text{W}(\text{N}_2)]_2$  complexes supported by I<sub>3</sub><sup>−</sup>, FeCl<sub>4</sub><sup>−</sup>, and tetracyanoethene (TCNE) anions was described, each with a characteristic dinitrogen stretching frequency at  $1988 \text{ cm}^{-1}$ . The X-band EPR spectrum of **W5** in 2-MeTHF glass at 20 K exhibited a rhombic signal with *g*-values of 2.76, 2.05, and 1.30, consistent with a  $S = 1/2$ , low-spin tungsten(I) compound (Figure 2a).<sup>33</sup> A values of 200 and 40 G for hyperfine coupling of <sup>31</sup>P and <sup>14</sup>N nuclei, respectively, provided the best fit. The solution-state magnetic susceptibility of **W5** was determined by Evan's method in THF-*d*<sub>8</sub> to be  $1.1(8) \mu_{\text{B}}$ , consistent with a low-spin W(I) complex.

The solid-state structure of **W5** was determined by X-ray diffraction using single crystals obtained from vapor diffusion of pentane into a concentrated diethyl ether solution at room temperature (Figure 2b). These data confirm the formation of an idealized octahedral, 17-electron tungsten bis(dinitrogen) complex,  $[\text{trans}-(\text{dppe})_2\text{W}(\text{N}_2)_2][\text{BARF}_4]$ .<sup>34</sup> The N≡N bond length of 1.134(9) Å, is statistically indistinguishable from the value of 1.126(15) Å reported for the neutral analogue, **W4**.<sup>35</sup> The similarity in N≡N bond distances is anticipated as oxidation results in loss of an electron from an essentially nonbonding *t*<sub>2g</sub>-type orbital. Likewise, the W–P bond lengths of 2.5077(15) and 2.5034(15) Å are similar to those reported in **W4** at 2.452(3), 2.466(3), 2.455(3), and 2.444(3) Å.

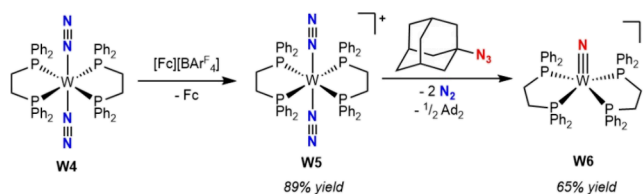
Attempts to promote N<sub>2</sub> cleavage from **W5** by allowing the compound to stand at ambient temperature for 24 h or heating to  $60^\circ\text{C}$  in THF were unsuccessful and produced no reaction. Irradiation of a diethyl ether solution of the compound with white LEDs or ultraviolet light for 12 h also produced no reaction. Because **W5** is monomeric, it is likely that the phenyl

**Scheme 3. Oxidation of  $(\text{dppe})_2\text{W}(\text{N}_2)_2$  to Form  $[(\text{dppe})_2\text{W}(\text{N}_2)_2][\text{BAR}^F_4]$** 

**A. X-Band EPR Spectrum of  $[(\text{dppe})_2\text{W}(\text{N}_2)_2][\text{BAR}^F_4]$  (W5)**

**B. Solid State Structure of  $[(\text{dppe})_2\text{W}(\text{N})][\text{BAR}^F_4]$  (W5)**


**Figure 2.** (a) EPR spectrum of W5 recorded at 20 K in 2-MeTHF solution (microwave frequency = 9.368 GHz, power = 2.000 mW, modulation amplitude = 4.000 g/100 kHz). (b) X-ray crystal structure of W5. Hydrogen atoms, solvent (diethyl ether), and disorder omitted for clarity. Ellipsoids presented with 30% probabilities.

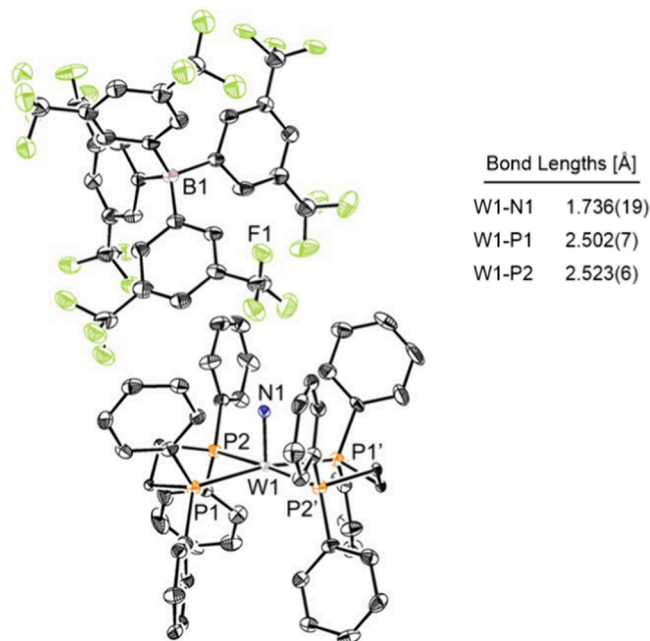
substituents sterically prevent formation of the bridged dinitrogen intermediate required for  $\text{N}_2$  cleavage.

The desired cationic tungsten(IV) nitride,  $[(\text{dppe})_2\text{WN}]^+$  (W6), was previously proposed by Tuzek and co-workers following the protonation of the tungsten dialkylhydrazido complex,  $(\text{dppe})_2\text{W}(\text{N}-\text{NC}_5\text{H}_{10})$ , with HLutBPh<sub>4</sub> with concomitant release of piperidine.<sup>36</sup> The independent synthesis of W6 was also accomplished by the addition of 1-azidoadamantane to a diethyl ether solution of W5 (Scheme 4). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of W6 in diethyl ether exhibits a

**Scheme 4. Synthesis of  $[(\text{dppe})_2\text{W}(\text{N})][\text{BAR}^F_4]$** 


singlet at 72.86 ppm with a characteristic  $^1J_{\text{PW}}$  coupling of 159 Hz. A singlet at 836 ppm was observed in the  $^{15}\text{N}$  NMR spectrum of W6- $^{15}\text{N}$  with  $^{183}\text{W}$  satellites of 25 Hz.

This downfield shift appears in a similar region with other W(IV) nitrides, such as the value of 787 ppm assigned for the 2,2'-( $^t\text{Bu}_2\text{As}$ )<sub>2</sub>-substituted tolane-supported nitride reported by Ballmann and co-workers (Scheme 1b).<sup>24</sup> Single crystals of W6 suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a concentrated solution of the nitride in diethyl ether. A representation of the solid-state structure is presented in Figure 3 and a  $\text{W}\equiv\text{N}$  bond length of 1.736(19) Å was observed, similar to the value in W3.

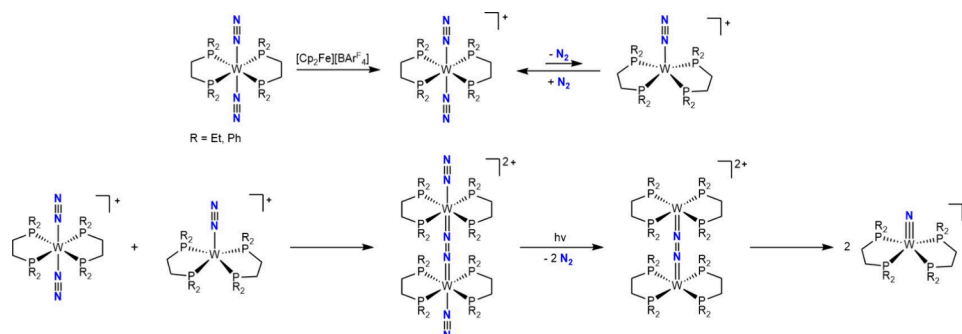


**Figure 3.** X-ray crystal structure of W6. Hydrogen atoms, solvent (pentane), and disorder omitted for clarity. Ellipsoids presented with 30% probabilities.

The synthesis of W3 by dinitrogen cleavage and the isolation of W5 and its inertness toward such reactivity supports the pathway for  $\text{N}_2$ -derived tungsten nitride formation illustrated in Scheme 5. One-electron oxidation of *trans*-( $\text{P}_2$ )<sub>2</sub>W( $\text{N}_2$ )<sub>2</sub> results in formation of the corresponding 17-electron, cationic tungsten bis(dinitrogen) compound. With appropriately sized phosphine substituents, dissociation of an  $\text{N}_2$  ligand enables formation of the bimetallic  $\mu_2$ -dinitrogen intermediate with two terminal  $\text{N}_2$  ligands. Unlike molybdenum where these ligands are thermally labile, irradiation with visible light is required with tungsten to access the requisite “zigzag” transition state en route to the W(IV) nitride product.

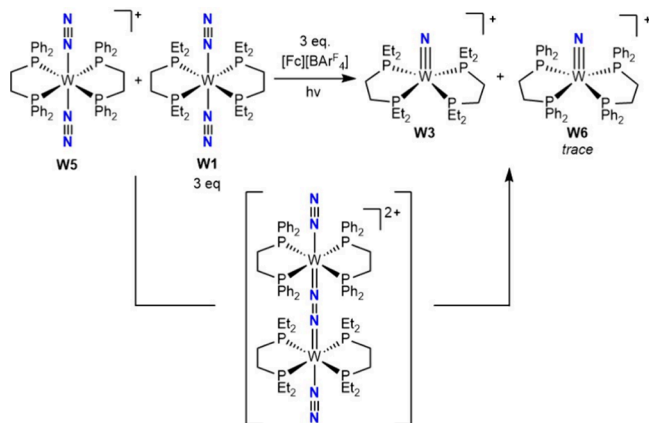
A mixing experiment was conducted to evaluate the feasibility of the proposed mechanism. While the phenyl

## Scheme 5. Proposed Mechanism for One-Electron Oxidation-Induced Dinitrogen Cleavage



substituents in **W5** were too large to form the bimetallic intermediate, mixing the dppe-supported tungsten compound with the depe variant may enable formation of the requisite  $\mu_2$ -dinitrogen ligand. Three equivalents of **W1** were added to one equivalent of **W5** generated *in situ*, followed by the addition of three equivalents of  $[\text{Cp}_2\text{Fe}][\text{BARF}_4]$  in THF- $d_8$  (Scheme 6).

## Scheme 6. Mixing Experiment to Support Bimetallic Bridge Formation in Dinitrogen Cleavage

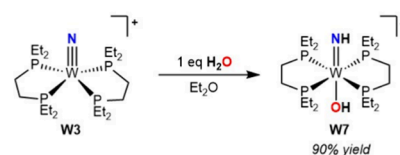
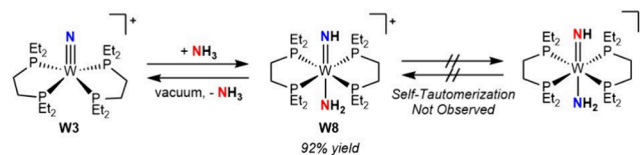


An excess of **W1** was added due to homodimerization and irreversible cleavage of the nonmixed bridge **W2** competing with potential formation of the mixed-bridge compound. Irradiation of the reaction, with white LEDs, yielded both tungsten nitrides, as judged by  $^{31}\text{P}$  NMR spectroscopy, indicating the intermediacy of the mixed-bridge compound in the reaction.

Reactivity of the  $\text{N}_2$ -Derived Tungsten(IV) Nitride

The reactivity of **W3** with water, ammonia, and dihydrogen was explored. While optimizing the synthesis of **W3**, it was determined that several undesired byproducts were removed by performing the photodriven cleavage in silylated glassware, consistent with the oxophilicity of the tungsten intermediates and products. This observation motivated experiments to determine the reactivity of **W3** with  $\text{H}_2\text{O}$  under controlled conditions.

One equivalent of water was added as a dilute stock solution in diethyl ether to a solution of **W3**, resulting in a color change from red to yellow, signaling formation of the cationic imido hydroxide compound,  $[(\text{depe})_2\text{W}(\text{NH})(\text{OH})][\text{BARF}_4]$  (**W7**, Scheme 7a). The THF- $d_8$   $^{31}\text{P}$  NMR spectrum exhibited a singlet at 33.80 ppm while broad peaks were located at 5.77 and 0.42 ppm in the  $^1\text{H}$  NMR spectrum corresponding to the

Scheme 7. Reactivity of  $[(\text{depe})_2\text{W}(\text{N})][\text{BARF}_4]$  with Water and AmmoniaA. Reactivity of  $[(\text{depe})_2\text{W}(\text{N})]^+$  towards  $\text{H}_2\text{O}$ B. Reactivity of  $[(\text{depe})_2\text{W}(\text{N})]^+$  towards  $\text{NH}_3$ 

protons in the imido and hydroxide ligands, respectively. Both O–H and N–H stretches were observed in the solid-state (KBr) infrared spectrum at 3696 and 3417  $\text{cm}^{-1}$ , respectively. A deuterium-enriched sample was prepared using  $\text{D}_2\text{O}$ , and it exhibited near identical shifts in the  $\text{Et}_2\text{O}$   $^2\text{H}$  NMR spectrum and isotopically shifted bands in the solid-state (KBr) IR spectrum at 2725 and 2542  $\text{cm}^{-1}$ .

The addition of  $\text{NH}_3$  to **W3** was also explored. An excess of ammonia ( $\sim 10$  equiv) was added to a THF- $d_8$  solution of **W3**, and a color change from red to yellow was observed, accompanied by complete conversion of the starting material (Scheme 7b). Analysis of the reaction mixture by  $^{31}\text{P}$  NMR spectroscopy in THF- $d_8$  revealed formation of a singlet at 29.65 ppm. This observation along with the appearance of broadened  $^1\text{H}$  NMR resonances at  $-1.25$  and 6.61 ppm in a 2:1 ratio was consistent with formation of  $[(\text{depe})_2\text{W}(\text{NH})(\text{NH}_2)]$  (**W8**). When the reaction was repeated using  $^{15}\text{NH}_3$  and natural abundance nitrogen in **W3**, the broadened  $^1\text{H}$  NMR resonance at  $-1.25$  ppm appeared as a doublet of quintets ( $^1J_{\text{NH}} = 65.9$  Hz,  $^3J_{\text{PH}} = 5.5$  Hz), supporting coupling of the proton to the  $^{15}\text{N}$  nuclei and the four  $^{31}\text{P}$  nuclei bound to tungsten. The lack of a broadened peak between the doublet of quintets implies that there is no self-tautomerization between the protons of the amido and imido ligands. It is likely that the broadening of the proton resonances in the natural abundance sample is a result of the quadrupolar  $^{14}\text{N}$  nucleus. Likewise, the lack of resolution on the broadened imido resonance further corroborates the absence of self-tautomerization. The  $^{15}\text{N}$  NMR spectrum, indirectly detected using an  $^{15}\text{N}$ – $^1\text{H}$  HSQC experiment, displayed only one resonance, observed at 21.3 ppm relative to  $\text{NH}_3$ , which

correlated with the amido  $^1\text{H}$  resonance. When  $\text{ND}_3$  was used, the resonances assigned to the amido and imido ligands on the  $^1\text{H}$  NMR were no longer observed with near identical peaks being observed in the  $^2\text{H}$  NMR spectrum. Notably, **W8** converted back to **W3** after extended exposure to active vacuum, demonstrating that the addition of ammonia is reversible.

Given previous reports of the hydrogenation of its molybdenum congener,  $[(\text{depe})_2\text{Mo}(\text{N})][\text{BAR}^{\text{F}}_4]$ ,<sup>9</sup> the hydrogenation of **W3** was explored to determine if established methods are capable of promoting the hydrogenation of the strong  $\text{W}\equiv\text{N}$  triple bond (Scheme 8). Using the conditions

**Scheme 8. Photodriven Hydrogenation of  $[(\text{depe})_2\text{W}(\text{N})][\text{BAR}^{\text{F}}_4]$  with  $\text{Ir}(\text{ppy})_3$**



previously optimized for the molybdenum congener,<sup>9</sup> irradiation of a THF solution of **W3** in the presence of 2.5 mol % of  $\text{Ir}(\text{ppy})_3$  with 440 nm blue LEDs under 4 atm of  $\text{H}_2$  produced  $\text{NH}_3$  in 21% yield. Control experiments established the decomposition of **W3** upon irradiation in the absence of  $\text{Ir}(\text{ppy})_3$  without generation of ammonia. The yield of ammonia was determined by vacuum transfer of the volatiles after the reaction to a side-arm flask containing excess 2 M  $\text{HCl}$  in diethyl ether to trap ammonia as ammonium chloride. Performing the hydrogenation in  $\text{THF-}d_8$  with  $\text{H}_2$  gas produced  $\text{NH}_3$  exclusively as judged by trapping with  $\text{BH}_3$  and analysis by NMR spectroscopy.

Analysis of the nonvolatile components by  $^{31}\text{P}$  NMR spectroscopy revealed a peak centered at 50.93 ppm corresponding to the tungsten pentahydride derivative,  $[(\text{depe})_2\text{WH}_5][\text{BAR}^{\text{F}}_4]$  (**W9**). This product, formed in 61% yield, also exhibited a quintet ( $^2J_{\text{PH}} = 30.7$  Hz) at  $-4.12$  ppm in the  $^1\text{H}$  NMR spectrum, consistent with hydride ligands split by four equivalent  $^{31}\text{P}$  nuclei. Independent synthesis of **W9** was accomplished by first synthesizing the neutral polyhydride,  $(\text{depe})_2\text{WH}_4$ , by photolysis of **W1** in the presence of dihydrogen. Protonation of  $(\text{depe})_2\text{WH}_4$  by addition of one equivalent  $[\text{H}(\text{OEt}_2)_2][\text{BAR}^{\text{F}}_4]$  in  $\text{THF-}d_8$  generated NMR signals identical to those observed following the hydrogenation of **W3**. Attempts to induce  $\text{N}_2$  cleavage from **W9** as was reported for the molybdenum congener either thermally or photochemically have been unsuccessful.

No remaining resonances in the  $^{31}\text{P}$  NMR spectrum of the hydrogenation reaction account for greater than 10% of the reaction mixture. **W7** was observed in 3% yield, and **W8** was not observed. Two doublets at 40.32 and 38.96 ppm were observed in 9 and 8% yields and are assigned as  $[(\text{depe})_2\text{W}(\text{NH})(\text{F})][\text{BAR}^{\text{F}}_4]$  and  $[(\text{depe})_2\text{W}(\text{O})(\text{F})][\text{BAR}^{\text{F}}_4]$ , resulting from photodegradation of the  $\text{BAR}^{\text{F}}_4$  anion. Free depe represents an additional 8% of the observed  $^{31}\text{P}$  containing products. Digestion of the nonvolatile mixtures with  $\text{H}_2\text{SO}_4$  failed to produce additional ammonium salts.

The hydrogenolysis reactivity of **W6** was also investigated to assess the influence of ligand environment on nitride reduction. Upon irradiation with blue LEDs under four atmospheres of dihydrogen, only trace amounts of ammonia

were detected. The nonvolatile components of the reaction mixture were intractable with no spectroscopic evidence for hydrogenation of the tungsten nitride. It is likely that the increased susceptibility of **W6** toward cyclometalation under photolytic conditions is responsible for the lack of productive hydrogenation reactivity. These observations are consistent with prior observations of cyclometalation in dppe-supported tungsten complexes when exposed to irradiative and hydrogenative conditions.<sup>37</sup>

Notably, the hydrogenation of **W3** demonstrates that a bisphosphine-supported tungsten(IV) nitride undergoes hydrogenation to generate ammonia and  $(\text{depe})_2\text{W}(\text{H})_5$  cationic products upon photoirradiation with  $\text{Ir}(\text{ppy})_3$ . This represents a rare example of ammonia generation from dihydrogen and a well-defined terminal tungsten nitride and demonstrates that even the recalcitrant  $\text{W}\equiv\text{N}$  bond is amenable to hydrogenation under photoirradiative conditions.

## CONCLUSIONS

The W(IV) nitride  $[(\text{depe})_2\text{W}(\text{N})][\text{BAR}^{\text{F}}_4]$  (**W3**) was generated by the cleavage of dinitrogen following one-electron oxidation and visible-light irradiation of  $(\text{depe})_2\text{W}(\text{N}_2)_2$  (**W1**), representing a rare example of dinitrogen cleavage leading to the formation of a W(IV) nitride. A dinitrogen bridging bimetallic intermediate (**W2**) was spectroscopically characterized and identified as *en route* to nitride generation. While this reactivity was facile in the case of **W1**, when the depe ligands are replaced by dppe ligands (**W4**),  $\text{N}_2$  cleavage was not observed. Instead, oxidation resulted in the formation of a 17-electron monometallic W(I) compound (**W5**), which is unable to form the requisite bridging intermediate to cleave dinitrogen due to steric repulsion. The corresponding nitride to **W4** has been independently synthesized using 1-azidoadamantane as the nitrogen source. A mechanism for one-electron oxidation-induced dinitrogen splitting is proposed and was probed through the formation of a mixed bridged compound. Hydrogenation of the  $\text{N}_2$ -derived nitride **W3** resulted in the release of free ammonia with concomitant generation of a tungsten pentahydride cation compound, **W9**. This represents a rare example of ammonia generation from dinitrogen with dihydrogen as a terminal reductant, and the first time this reactivity has been observed on a well-defined tungsten nitride.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.5c00533>.

Experimental details including the preparation of tungsten complexes; UV–vis monitoring of photodriven dinitrogen splitting; photodriven hydrogenation; additional spectroscopic data; and X-ray crystallography (PDF)

Crystallographic data (CIF)

### Accession Codes

Deposition Numbers 2447410–2447412 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe: <https://www.ccdc.cam.ac.uk/structures/>.

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## Notes

The authors declare no competing financial interest.

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