Functionalization of N₂ to NH₃ via direct N ≡ N bond cleavage using M(III)(NMe₂)₃ (M=W/Mo): A theoretical study

SAMBATH BASKARAN, PERUMAL BALU and CHINNAPPAN SIVASANKAR*

Catalysis and Energy Laboratory, Department of Chemistry, Pondicherry University, R. V. Nagar, Puducherry 605 014, India
e-mail: siva.che@pondiuni.edu.in

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Abstract. Atmospheric N₂ can be cleaved directly to yield metal-nitride (before proceeding to the functionalization of N_α of coordinated N₂) and subsequently functionalized to ammonia using M(III)(NMe₂)₃ (M = W/Mo) as a catalyst, and suitable proton and electron sources. The calculated energies of thermodynamic and kinetic states of the various intermediates and transition states in the reaction coordinate to yield ammonia confirmed the viability of the proposed reaction pathway. Rationale of different pathways have been examined and discussed in detail. Changes in the structural features of the catalyst and some important intermediates and transition states have also been examined.

Keywords. Dinitrogen; nitride; nitrogen fixation; ammonia; tungsten.

1. Introduction

Converting N₂ to ammonia through cleavage of N≡N triple bond has long been a challenging task in the field of inorganic chemistry.^{1–13} Nitrogenase enzyme reduces the atmospheric N₂ to ammonia by stepwise additions of protons and electrons at ambient temperature and pressure.^{14–24} Allen and Senoff synthesized the first water soluble dinitrogen complex, [Ru(NH₃)₅N₂]²⁺ in 1965, which failed to produce ammonia under employed experimental conditions.²⁵ Chatt *et al.* have reported the synthesis and reactivity of [M(dppe)₂(N₂)₂] (M = Mo/W) some dinitrogen complexes by stepwise addition of protons and electrons to produce ammonia (scheme 1).²⁶ Schrock *et al.* have reported a Mo^{III}-triamidoamine dinitrogen complex which produces ammonia catalytically in the presence of Cp*₂Cr (Cp* = C₅Me₅) and LutH⁺ (Lut = 2,6-dimethylpyridine) in heptane and followed the Chatt-type mechanism.²⁷ In the recent past, Nishibayashi *et al.* reported some Mo complexes of PNP-based pincer type ligands [Mo(N₂)₂(PNP)(μ-N₂)] to produce ammonia from N₂ in the presence of Cp₂Co and LutH⁺ at ambient conditions.²⁸ Our group recently reported a new strategy for hydrogenation of dinitrogen into ammonia using organic co-catalysts by DFT calculation.^{29–32} In all the above mentioned processes, first the β-Nitrogen is converted to ammonia and generate the metal nitride

complex and the nitride complex further reacted with protons and electrons to produce second equivalent of ammonia.

Fryzuk and Chirik co-workers independently reported the hydrogenation of dinitrogen using molecular hydrogen and Zr-based transition metal catalyst.^{33,34} Holthausen, Schneider and co-workers reported a PNP type pincer ligand-based ruthenium-nitrido ((PNP)Ru≡N) complex which reacts with molecular hydrogen under mild reaction conditions to yield ruthenium-hydrido complex and 80% ammonia.³⁵ Burger and co-workers have reported the hydrogenation of iridium-nitrido complex to yield corresponding amido complex, however it failed to produce ammonia.³⁶ Meyer Smith and co-workers have reported a synthesis and reactivity of tripodal NHC ligand-based tetra-coordinated iron(v)-nitrido complex which produced ammonia at –78°C in THF along with iron(II) complex.³⁷

On the other hand, experimentally only Holland *et al.* reported the reaction of (NACNAC)FeCl₂ (NACNAC=MeC[C(Me)N(2,6-Me₂C₆H₃)]₂) with N₂ in the presence of potassium as a reductant to yield corresponding nitride complex via direct N-N bond cleavage. More interestingly, this nitride complex produced ammonia by reaction with ethereal HCl (82±4% yield).³⁸

Except Holland's report, all the above discussed metal-nitride complexes were mainly prepared from the reaction of azide with the corresponding metal

*For correspondence

Scheme 1. Stepwise functionalization of N_2 .

precursors (eq. 1) and not from N_2 . At this juncture, it is worth mentioning that not much research has been done for the reduction of nitride complexes generated from direct $N\equiv N$ bond cleavage of N_2 and subsequently to produce ammonia (scheme 2).

Cummins, Laplaza and co-workers reported the reductive cleavage of dinitrogen into nitrido ligand in the presence of $Mo(III)(NRAr)_3$, where R is $C(CD_3)_2CH_3$ and Ar is $3,5-C_6H_3(CH_3)_2'$, at ambient temperature.³⁹ Many theoretical studies have been reported to explain the structure and reactivity of metal-nitride complexes.^{40–44} Morokuma *et al.* reported that the tungsten triamido complex would be the best for the

formation of metal nitride from N_2 than the molybdenum triamido complex.⁴⁴ However, no report is available for the reactivity of Cummins nitride complex with protons and electrons to yield ammonia. One of the reasons why Cummins nitride complex failed to produce ammonia is that the ancillary ligand stabilized the metal nitride to the great extent. Recently McElwee-White *et al.* synthesized and structurally characterized tungsten nitrido complex $(NW(NMe_2)_3)$.^{45,46} In this regard, herein we report a suitable metal complex with appropriate ancillary ligands to directly cleave N_2 to form metal-nitride complex, which subsequently reacted with protons and electrons to yield ammonia.

2. Computational Details

Complexes **1–10**, **5a**, **8a**, **11a** and **TS-I**, **TS-II**, **TS-III** have been fully optimized at B3LYP^{47–49} level of theory using LANL2DZ basis set.^{50–53} Vibrational frequency calculations were performed on these optimized structures to confirm the stationary points. A solvent correction (for Heptane, Toluene and THF) was performed using the polarized continuum model (PCM),^{54–56} natural population analysis (NPA) was performed using same level of theory and basis set. A natural bond orbital analysis (NBO) was carried out to understand more about the electronic structure of the model systems. All these computational procedures were used as implemented in the Gaussian 03 package.⁵⁷

3. Results and Discussion

3.1 Functionalization of nitride to ammonia using tungsten complex

Geometry optimizations and frequency calculations were carried out for the complexes **1–10**, **5a**, **8a**, **11a**, and **TS-I**, **TS-II**, **TS-III**. The energies and selected optimized structural parameters of the model systems presented in tables 1 and 2 and illustrated in figures 1 and 2. In the present study we used $[LutH]^+$ ($Lut = 2, 6$ -dimethyl pyridine) and $[Cp^*_2Cr]$ ($Cp^* = C_5Me_5$) as proton and electron sources for the functionalization of nitride to ammonia as proposed in the schemes 3 and 4. We have attempted to use the nitride complex which is generated from the direct $N\equiv N$ bond cleavage of N_2 to produce ammonia in the presence of suitable proton and electron sources as proposed in the scheme 2. We have carefully chosen dimethyl amide as an ancillary ligand to have balanced energy profile to achieve the catalytic cycle. The dimethyl amide based W/Mo

Scheme 2. The proposed catalytic cycle for the ammonia formation via nitride formation by direct cleavage of $N\equiv N$.

Table 1. Calculated energies and spin states for tungsten model systems **1-10, 5a, 8a, 11a** and **TS-I, TS-II, TS-III**.

Systems	Spin States	Energy [Hartree]	Entropy (cal/mol/K)	ZPE (Hartree)	Solvation (kcal/mol)		
					Heptane	Toluene	THF
[W]	(1) $S = 1/2$	-471.4710032	133.061	0.245974	-1.01	-1.39	-3.37
[W]-N $\equiv$ N	(2) $S = 1/2$	-581.007419	139.753	0.254137	-2.26	-3.04	-6.45
[W]-N $\equiv$ N-[W]	(3) $S = 0$	-1052.5712012	225.650	0.501400	-0.42	-0.59	-1.20
[W] $\equiv$ N	(4) $S = 0$	-526.318809	131.840	0.250880	-2.63	-3.46	-7.27
[W]=NH $^+$	(5) $S = 0$	-526.722705	134.922	0.263119	-19.07	-23.21	-35.59
[W]=NH	(6) $S = 1/2$	-526.8931317	134.827	0.260484	-1.40	-1.83	-2.19
[W]-NH $_2^+$	(7) $S = 1/2$	-527.3158407	137.200	0.275010	-19.11	-23.33	-35.82
[W]-NH $_2$	(8) $S = 0$	-527.4837282	129.444	0.271961	-0.86	-1.13	-2.19
[W]-NH $_3^+$	(9) $S = 0$	-527.882556	150.221	0.287309	-20.27	-24.82	-38.74
[W]-NH $_3$	(10) $S = 1/2$	-528.0220294	140.377	0.285628	-2.39	-3.13	-6.56
[W] $\equiv$ N] $^+$	(5a) $S = 0$	-526.7044706	131.196	0.266614	-20.93	-25.73	-41.16
[W]=NH $^+$	(8a) $S = 1/2$	-527.2914719	135.435	0.276613	-20.14	-24.62	-38.45
[W]=NH $_2^+$	(11a) $S = 0$	-527.8830556	135.554	0.287760	-20.09	-24.61	-38.70
[W] $\equiv$ N] $^+$	(TS-I) $S = 0$	-526.6158674	131.210	0.258627	-24.96	-30.61	-48.78
[W]=NH $^+$	(TS-II) $S = 1/2$	-527.2381522	135.432	0.270337	-23.51	-28.86	-45.18
[W]=NH $_2^+$	(TS-III) $S = 0$	-527.8420035	133.163	0.282696	-23.45	-28.72	-44.77
N $_2$		109.4808546	45.885	0.005165	-0.87	-0.48	-0.37
NH $_3$		-56.5480839	44.443	0.033179	-3.05	-1.69	-1.32
[Cp* $_2$ Cr] $^+$		-866.2178567	179.281	0.447136	-15.89	-19.31	-29.42
[Cp* $_2$ Cr]		-866.3221052	171.110	0.446483	-0.53	-0.70	-1.54
[LutH] $^+$		-327.259668	91.264	0.158685	-23.93	-29.21	-45.35
[Lut]		-326.8692532	88.087	0.144391	-1.58	-2.23	-4.60

monomer (M(III)(NMe $_2$) $_3$) complexes are well reported in the literature, nevertheless the monomer is known to form dimeric complex (M $_2$ (NMe $_2$) $_6$).⁵⁸

The calculated thermodynamic energy profile is given in figure 3. The reaction of [W(NMe $_2$) $_3$] (1) with dinitrogen to yield complex 2 ([W-N $_2$ (NMe $_2$) $_3$]) is

Table 2. Bond lengths, bond angles and vibrational frequency of Tungsten model systems **1-10, 5a, 8a, 11a** and **TS-I, TS-II, TS-III**.

Systems		Bond Length (Å)			Bond Angle (°)	Vibrational frequency (cm $^{-1}$)		NPA		WBI	
		W-N _(amide)	W-N	N-N		W-N	N-N	W	N	W-N	N-N
[W]	(1)	1.95	—	—	—	—	—	1.00	—	0.94	—
[W]-N $_{\alpha}$ $\equiv$ N $_{\beta}$	(2)	1.96	1.89	1.20	173.3	522	1703	1.46	N $_{\alpha}$ = -0.32 N $_{\beta}$ = -0.12	1.04	2.17
[W]-N $\equiv$ N-[W]	(3)	1.96	1.84	1.24	164.7	778	1604	1.53	-0.45	1.29	1.52
[W] $\equiv$ N	(4)	1.97	1.70	—	—	1111	—	1.57	-0.58	2.60	—
[W]=NH $^+$	(5)	1.93	1.74	—	—	1033	—	1.79	-0.79	1.98	—
[W]=NH	(6)	1.97	1.78	—	—	941	—	1.66	-0.99	1.74	—
[W]-NH $_2^+$	(7)	1.92	1.93	—	—	719	—	1.85	-0.55	0.99	—
[W]-NH $_2$	(8)	1.97	1.96	—	—	668	—	1.51	-1.15	0.94	—
[W]-NH $_3^+$	(9)	1.92	2.29	—	—	353	—	1.24	-1.10	0.32	—
[W]-NH $_3$	(10)	1.98	2.31	—	—	270	—	1.08	-1.08	0.30	—
[W] $\equiv$ N] $^+$	(5a)	1.93	1.69	—	—	1123	—	1.54	-0.49	2.64	—
[W]=NH $^+$	(8a)	1.95	1.76	—	—	998	—	1.62	-0.86	1.94	—
[W]=NH $_2^+$	(11a)	1.92	1.94	—	—	668	—	1.39	-1.10	1.06	—
[W] $\equiv$ N] $^+$	(TS-I)	1.92	1.74	—	—	1023 (W-N) -1811 (TS-I)	—	1.67	-0.63	2.21	—
[W]=NH $^+$	(TS-II)	1.92	1.86	—	—	833 (W-N) -1684 (TS-II)	—	1.73	-1.00	1.42	—
[W]=NH $_2^+$	(TS-III)	1.90	2.14	—	—	606 (W-N) -1452 (TS-III)	—	1.38	-1.20	0.54	—

Figure 1. Optimized geometries of tungsten model systems 1–10.

found to be exergonic by 22 kcal mol⁻¹, 22 kcal mol⁻¹ and 24 kcal mol⁻¹ (Heptane, Toluene and THF respectively). The subsequent reaction of complex **1** $[\text{W}(\text{NMe}_2)_3]$ with complex **2** to yield binuclear dinitrogen complex **3** $[(\text{Me}_2\text{N})_3\text{W-N}\equiv\text{N-W}(\text{NMe}_2)_3]$ is calculated to be exergonic by 41 kcal mol⁻¹, 40 kcal mol⁻¹ and 35 kcal mol⁻¹ (Heptane, Toluene and THF respectively). We have also attempted to calculate the energy barrier for the dimerization of $\text{W}(\text{NMe}_2)_3$ (**1**) and found to be highly exergonic by 72 kcal mol⁻¹, 71 kcal mol⁻¹ and 67 kcal mol⁻¹ in Heptane, Toluene and THF respectively. This finding indicates that the dimerization is also feasible for the complex **1**. Nevertheless, the dinitrogen binding cannot be ignored since this particular reaction is also exergonic in nature.

The conversion of complex **3** $[(\text{Me}_2\text{N})_3\text{W-N}\equiv\text{N-W}(\text{NMe}_2)_3]$ to form two equivalent of W-nitride

complex **4** $[(\text{NMe}_2)_3\text{W}\equiv\text{N}]$ through N≡N bond cleavage is found to be more exergonic by 58, 59 and 66 kcal mol⁻¹ (Heptane, Toluene and THF respectively) and the calculated barriers are comparable with the Morokuma's report. Nevertheless, our nitride complex **4** is not as stable as previously reported nitride,⁴⁴ therefore complex **4** can react further with suitable reagents to yield ammonia. Protonation of complex **4** $[(\text{NMe}_2)_3\text{W}\equiv\text{N}]$ by $[\text{LuH}]^+$ to form complex **5** $[(\text{Me}_2)_3\text{N}]\text{W=NH}^+$ is calculated to be exergonic by 4, 2 kcal mol⁻¹ in Heptane and Toluene respectively and endergonic by 3 kcal mol⁻¹ in THF. Further reduction of complex **5** $[(\text{Me}_2)_3\text{N}]\text{W=NH}^+$ using $[\text{Cp}^*_2\text{Cr}]$ to yield complex **6** $[(\text{Me}_2)_3\text{N}]\text{W=NH}$ is calculated to be exergonic by 38, 38 and 35 kcal mol⁻¹ (Heptane, Toluene and THF respectively). Addition of $[\text{LuH}]^+$ to the complex **6** $[(\text{Me}_2)_3\text{N}]\text{W=NH}$ to yield complex

Figure 2. Optimized geometries of tungsten model systems **5a**, **8a**, **11a**, **TS-I**, **TS-II** and **TS-III**.

7 ($[(Me_2)_3N]W-NH_2]^+$) is found to be exergonic by 15, 14 and 13 kcal mol⁻¹ (Heptane, Toluene and THF respectively). Subsequent reduction of complex **7** to produce complex **8** ($[(Me_2)_3N]W-NH_2$) is also calculated to be highly exergonic by 39, 38 and 36 kcal mol⁻¹ (Heptane, Toluene and THF respectively) (figure 3). The protonation of complex **8** using $[LutH]^+$ to yield complex **9** ($[(Me_2)_3N]W-NH_2^+$) is found to be exergonic by 7, 7 and 6 kcal mol⁻¹ (Heptane, Toluene and THF respectively). The reduction of complex **9** by $[Cp^*_2Cr]$ to yield complex **10** ($[(Me_2)_3N]W-NH_3$) is calculated to be exergonic by 20, 19 and 18 kcal mol⁻¹ (Heptane, Toluene and THF respectively). Finally, the replacement of ammonia in complex **10** to regenerate the complex **1** ($[W(NMe_2)_3]$) is calculated to be exergonic by 15, 13 and 11 kcal mol⁻¹ (Heptane, Toluene

and THF respectively). The calculated thermodynamic barriers show that the formation of ammonia from dinitrogen using complex **1** in Heptane is more feasible than in Toluene and THF. All the thermodynamic steps and kinetic steps involved in the catalytic cycle in Heptane can be accessed energetically and therefore it may be experimentally feasible to achieve ammonia production using $(Me_2N)_3W$ and N_2 .

We have attempted to protonate the dinitrogen in complex **2** ($[(NMe_2)_3W-N_2]$) with $[LutH]^+$ and found to be slightly endergonic by 4 kcal mol⁻¹, 5 kcal mol⁻¹ and 9 kcal mol⁻¹ (Heptane, Toluene and THF respectively) (eq. 2). This finding indicates that the dimerization (formation of complex **3**, -41 kcal mol⁻¹, -40 kcal mol⁻¹ and -35 kcal mol⁻¹) is more feasible than the protonation on dinitrogen in complex **2**

($[(\text{NMe}_2)_3\text{W-N}_2]$). Nevertheless, this possibility cannot be ruled out completely.

We have also investigated different pathways for functionalizing the N_2 to NH_3 (scheme 4). The possibility of protonation on one of the amide nitrogens (ancillary ligands) to form dimethyl ammonia bound complex **5a** ($[(\text{NMe}_2)_2(\text{NHMe}_2)\text{W}\equiv\text{N}]^+$) and subsequent transfer of proton to the nitride via four member transition state (figures 4–6) have been examined owing to the known literature precedent for similar situation where few experimental and theoretical reports are available for the protonation on the amide nitrogen during the dinitrogen reduction into ammonia in $[\text{HIPTN}_3\text{N}]\text{Mo}^{\text{III}}-\text{N}\equiv\text{N}$ (HIPT = HIPT = 3,5-(2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$) $_2\text{C}_6\text{H}_3$) complex.^{59–61} The first protonation of amide nitrogen in complex **4** ($[(\text{NMe}_2)_3\text{W}\equiv\text{N}]$) by $[\text{LutH}]^+$ to yield complex **5a** ($[(\text{NMe}_2)_2(\text{NHMe}_2)\text{W}\equiv\text{N}]^+$) is endergonic by 9, 10 and 12 kcal mol $^{-1}$ (Heptane, Toluene

and THF respectively). And the formation of **TS-I** from the complex **5a** ($[(\text{NMe}_2)_2(\text{NHMe}_2)\text{W}\equiv\text{N}]^+$) is endergonic by 47, 46 and 43 kcal mol $^{-1}$ (Heptane, Toluene and THF respectively). The proton migration from amide nitrogen to nitride to yield complex **6** ($[(\text{NMe}_2)_3\text{W}=\text{NH}]^+$) is exergonic by 59, 58 and 52 kcal mol $^{-1}$ (Heptane, Toluene and THF respectively). The second protonation of amide nitrogen in complex **7** ($[(\text{NMe}_2)_3\text{W}=\text{NH}]$) to yield complex **8a** ($[(\text{NMe}_2)_2(\text{NHMe}_2)\text{W}=\text{NH}]^+$) is slightly endergonic (1, 1 and 1 kcal mol $^{-1}$ Heptane, Toluene and THF respectively). Further, the proton migration from complex **8a** ($[(\text{NMe}_2)_2(\text{NHMe}_2)\text{W}=\text{NH}]^+$) through **TS-II** to yield complex **9** ($[(\text{NMe}_2)_3\text{W}=\text{NH}_2]^+$) is exergonic by 42, 41 and 37 kcal mol $^{-1}$ (Heptane, Toluene and THF respectively). The addition of third equivalent of $[\text{LutH}]^+$ to the amide nitrogen of complex **10** ($[(\text{NMe}_2)_3\text{W}=\text{NH}_2]$) to yield complex **11a** ($[(\text{NMe}_2)_2(\text{NHMe}_2)\text{W}-\text{NH}_2]^+$) is exergonic by 2, 2 and 1 kcal mol $^{-1}$ (Heptane, Toluene and THF respectively). The formation of **TS-III** from complex **11a** ($[(\text{NMe}_2)_2(\text{NHMe}_2)\text{W}-\text{NH}_2]^+$) is endergonic by 20, 19 and 17 kcal mol $^{-1}$ and the subsequent intra molecular proton migration from **TS-III** to yield complex **12** ($[(\text{NMe}_2)_3\text{W}=\text{NH}_3]^+$) is exergonic by 24, 24 and 22 kcal mol $^{-1}$ (Heptane, Toluene and THF respectively). These findings indicate that the protonation on

Scheme 3. The proposed mechanism for the functionalization of N_2 in $[\text{M}(\text{NMe}_2)_3\text{N}_2]$ (**2**) ($\text{M} = \text{W}$ and Mo) (nitride protonation).

Scheme 4. The proposed mechanism for the functionalization of N_2 in $[M(NMe_2)_3N_2]$ (**2**) ($M = W/Mo$) (amide protonation).

nitride is more feasible than the protonation on the amide nitrogen of the ancillary ligand.

We have also carried out similar calculations for Molybdenum-nitride (figures S1 and S2) in the presence of $[LutH]^+$ and $[Cp^*_2Cr]$ in Heptane, Toluene and THF under normal experimental conditions, and observed a feasible situation for the reduction of nitride to ammonia (figure 7 and figures S3–S5). A comparison of all calculated thermodynamic barriers of $[(Me_2N)_3W]$ and $[(Me_2N)_3Mo]$ reaction with N_2 to produce ammonia in the presence of $LutH^+$ and Cp^*_2Cr revealed that the $[(Me_2N)_3W]$ would be the better choice than the $[(Me_2N)_3Mo]$.

We have also optimized all the systems in triplet and quartet spin states and compared the energies with singlet and doublet spin states. The energies are given in tables S3 and S4. The calculated energies from singlet and doublet spin states are more stabilized than the systems optimized with triplet and quartet spin states. The total energies revealed that the formation of ammonia from complex **1** from singlet and doublet spin states is more feasible than the triplet and quartet spin states. However, the energies of singlet and doublet spin states of systems **1**, **9**, **10**, **11a** and

TS-III are comparable with triplet and quartet spin states.

3.2 Wiberg bond indices (WBI)

In order to gain more insight to understand the electronic structure of all the intermediates formed during the course of the reaction, we have carried out the WBI calculations. The WBI of N-N bond in complex **2** ($[(Me_2N)_3W-N\equiv N]$) is found to be 2.17 and reveals more degree of activation (WBI for the free $N\equiv N$ is 3.00). In complex **3** ($[(Me_2N)_3W-N\equiv N-W(NMe_2)_3]$), the WBI of W-N bond is increased from 1.04 (in complex **2**) to 1.29 and the WBI of N-N bond is decreased from 2.17 to 1.52. These values suggest that the W-N bond interaction is increased in complex **3** when compared to complex **2** and the N-N bond becomes further weak owing to the electron density transferred from metal t_{2g} orbital to π^* orbital of N_2 ligand (back donation).

In complex **4** ($[(Me_2N)_3W\equiv N]$), the WBI of W-N bond increases from 1.29 to 2.60 owing to the increase in the orbital overlap and electron population in W-N bond. This observation clearly shows that the metal nitrogen interaction is increased significantly. During the

Figure 3. Calculated thermodynamic energy profile for the formation of ammonia from $[\text{W}(\text{NMe}_2)_3]$ (**1**) and N_2 in Heptane, Toluene and THF.

protonation of complex **4** with $[\text{LutH}]^+$ to give complex **5** $[(\text{Me}_2\text{N})_3\text{W-NH}]^+$, the WBI of W-NH bond interaction is decreased from 2.60 to 1.98 due to the conversion of nitride to imide. The reduction of complex **5** $[(\text{Me}_2\text{N})_3\text{W-NH}]^+$ using $[\text{Cp}^*\text{Cr}]$ to yield complex **6** $[(\text{Me}_2\text{N})_3\text{W-NH}]$, the WBI of W-NH bond interaction is further decreased from 1.98 to 1.74 which indicates that the W-N interaction in complex

6 becomes further weak. Protonation of complex **6** $[(\text{Me}_2\text{N})_3\text{W-NH}]$ using $[\text{LutH}]^+$ to form complex **7** $[(\text{Me}_2\text{N})_3\text{W-NH}_2]^+$ results in the decrease of WBI of W-NH₂ bond further from 1.74 to 0.99 owing to the formation of amido complex. In complex **8** $[(\text{Me}_2\text{N})_3\text{W-NH}_2]$, the WBI of W-NH₂ bond is further decreased from 0.99 to 0.94. Further protonation of complex **8** to yield complex **9** $[(\text{Me}_2\text{N})_3\text{W-NH}_3]^+$, the WBI of

Figure 4. Calculated thermodynamic energy profile for the formation of ammonia from $[\text{W}(\text{NMe}_2)_3]$ (**1**) and N_2 (via amide nitrogen protonation) in Heptane.

Figure 5. Calculated thermodynamic energy profile for the formation of ammonia from $[W(NMe_2)_3]$ (**1**) and N_2 (via amide nitrogen protonation) in Toluene.

W-NH₃ bond is decreased from 0.93 to 0.31 and the reduction of complex **9** using $[Cp^*_2Cr]$ to yield complex **10** $[(Me_2N)_3W-NH_3]$ further decreased the WBI of W-NH₃ bond from 0.31 to 0.29, and reveals the weak nature of interaction of ammonia with W which can be readily replaced by N_2 .

3.3 Changes in the structural features of complexes 1–10 during the course of the reaction

In complex **1** $[(Me_2N)_3W]$, the W-N bond distance is calculated to be 1.95 Å. In complex **2** $[(Me_2N)_3W-N_\alpha \equiv N_\beta]$, the W-N(N_2) bond distance is found to be

Figure 6. Calculated thermodynamic energy profile for the formation of ammonia from $[W(NMe_2)_3]$ (**1**) and N_2 (via amide nitrogen protonation) in THF.

Figure 7. Calculated thermodynamic energy profile for the formation of ammonia from $[\text{Mo}(\text{NMe}_2)_3]$ (**1**) and N_2 in Heptane, Toluene and THF.

1.89 Å. The N-N bond length in complex **2** is found to be 1.20 Å, while free N-N bond distance is 1.09 Å and indicates that the bonded N_2 is activated significantly by the electron transfer from t_{2g} set orbital of W to the π^* orbital of N_2 and the W-N-N bond angle is found to be 173.3° . In complex **3** $[(\text{Me}_2\text{N})_3\text{W}-\text{N}\equiv\text{N}-\text{W}(\text{NMe}_2)_3]$, the W-N bond length is decreased from 1.96 Å to 1.85 Å but the N-N bond distance is increased from 1.20 Å to 1.26 Å owing to the significant amount of activation of N_2 and the W-N-N bond angle is found to be 164.7° which further confirms that more activation of N_2 is related to the free dinitrogen. In complex **4** $[(\text{Me}_2\text{N})_3\text{W}\equiv\text{N}]$, the W-N bond length is calculated to be 1.70 Å, which is comparable with the similar metal nitride complexes.⁴⁴ The protonation of nitride ligand using $[\text{LutH}]^+$ in complex **4** to give complex **5** $[(\text{Me}_2\text{N})_3\text{W}=\text{NH}]^+$, the W-NH bond distance is increased from 1.70 Å to 1.74 Å. In complex **6** $[(\text{Me}_2\text{N})_3\text{W}=\text{NH}]$, the W-NH bond length is increased from 1.74 Å to 1.78 Å. In complex **7** $[(\text{Me}_2\text{N})_3\text{W}-\text{NH}_2]^+$, the bond length of W-NH₂ is increased from 1.78 Å to 1.93 Å, when complex **7** is reduced to complex **8** $[(\text{Me}_2\text{N})_3\text{W}-\text{NH}_2]$, the bond length of W-NH₂ bond is increased from 1.93 Å to 1.96 Å. In complex **9** $[(\text{Me}_2\text{N})_3\text{W}-\text{NH}_3]^+$, the W-NH₃ bond length is increased from 1.96 Å to 2.29 Å owing to the formation of ammonia which interacts with the metal centre relatively in a weak manner. In complex **10** $[(\text{Me}_2\text{N})_3\text{W}-\text{NH}_3]$, the W-NH₃ bond length is increased further from 2.29 Å to 2.32 Å.

4. Conclusions

In the present investigation, we have demonstrated theoretically that N_2 can be cleaved directly to produce metal-nitride which subsequently functionalized to ammonia in the presence of suitable transition metal catalyst. We have carefully chosen the Me_2N^- as an ancillary ligand to stabilize the N_2 complexes of W(III)/Mo(III). Our choice of ancillary ligand further helped us to stabilize the Mo(VI)-nitride complex moderately so that it could react further with protons and electrons to yield ammonia without much thermodynamic and kinetic barriers. We also observed that the $(\text{Me}_2\text{N})_3\text{M}-\text{N}\equiv\text{N}$ (**2**) preferred the formation of dinuclear complex $((\text{Me}_2\text{N})_3\text{M}-\text{N}\equiv\text{N}-\text{M}(\text{NMe}_2)_3)$ (**3**) over protonation on N_α in complex **1**. Preference for the formation of complex **3** is the key step to proceed to the formation of M(VI)-nitride (**4**). All the calculated barriers indicate that ammonia formation via direct $\text{N}\equiv\text{N}$ bond cleavage of N_2 , using our choice of catalysts and other mentioned reagents, seems to be viable.

Supplementary Information

Optimized geometries of Mo complexes, energy profiles, tables and Cartesian coordinates for reactants, products, intermediates and transition states are given in Supplementary Information which is available at www.ias.ac.in/chemsci.

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