A Model for Protonation of Dinitrogen by Nitrogenase: Protonation of Coordinated Dinitrogen on Tungsten with Hydrosulfido-Bridged Dinuclear Complexes[1]

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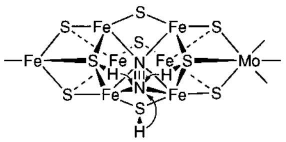
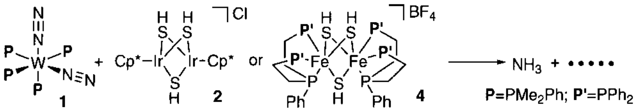
The mechanism for biological nitrogen fixation remains unclear although the X-ray structural model has recently been reported for the FeMo-cofactor of FeMo nitrogenase.[2] It has been made clear that the site where dinitrogen (N_2) is activated and reduced is an Fe/Mo sulfido cluster.[2] However, we are still uncertain about which metal is responsible for binding N_2.[2−4] Several groups claimed that protonation of the activated N_2 proceeds with the aid of the bridging hydrosulfido ligands in the cluster.[2d,3c−g,4] In Dance's model,[3c−g] the bridging sulfido ligands mediate proton transfer to the coordinated N_2 bound to the Fe_4 face of the Fe/Mo sulfido cluster via μ-SH intermediates as shown in Chart 1.

Up until now, many mononuclear and polynuclear N_2 complexes of transition metals have been prepared,[5] some of which liberate NH_3 and/or hydrazine (NH_2NH_2) by protonolysis with inorganic acids such as H_2SO_4. Typically, molybdenum and tungsten N_2 complexes of the type $M(N_2)_2(PMe_2Ph)_4$ (M = Mo, W) produce NH_3 and/or NH_2NH_2 in good yields by treatment with inorganic acids.[5a,6] Previously, the reactions of organic thiols or H_2S with those N_2 complexes were investigated, where H_2 gas was evolved and no N−H bond formation was observed.[7,8] This indicates that organic thiols and H_2S attack the electron-rich metal center in the N_2 complexes in place of the coordinated N_2. Very recently, we have reported the formation of NH_3 by ruthenium-assisted protonation of N_2 on W atom with H_2 under mild conditions.[9] As an extension of this multimetallic approach for nitrogen fixation, the reactivity of dinuclear complexes containing bridging hydrosulfido ligands toward coordinated N_2 was investigated and a series of hydrosulfido-bridged dinuclear compounds of ruthenium, iridium, and rhodium were prepared by our group, which served as versatile precursors for synthesis of various polynuclear sulfido clusters.[10] Interestingly, the proton on the bridging sulfur has been found to be transferred to the ligating N_2 to form NH_3. Preliminary results about these reactions will be described here.

Chart 1



Scheme 1



Treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**) with 10 equiv of $[Cp^*Ir(\mu\text{-}SH)_3IrCp^*]Cl$[10c] (**2**; Cp* = η^5-C_5Me_5) under nitrogen atmosphere in dichloroethane−benzene at 55 °C for 24 h afforded NH_3 in 78% total yield based on the W atom (Scheme 1). Free NH_3 in 3% yield was observed in the reaction mixture, and further NH_3 in 75% yield was released after base distillation. A longer reaction time improved the total yield of NH_3. The reaction also proceeded at 30 °C; however, the yield of NH_3 was lower. In the absence of **2**, no NH_3 was obtained. In all the cases, only a trace amount of NH_2NH_2 was observed. The typical results were shown in Table 1. The ^1H and ^{31}P NMR spectra of the reaction mixture showed the complete conversion of the N_2 complex and liberation of free PMe_2Ph from the W atom; however, neither tungsten products nor iridium products could be characterized. Because plausible hydrazido(2-) intermediate complexes, which might provide NH_3 by base treatment, were not detected by the NMR and IR spectra of the reaction mixture, we consider that protonation of the coordinated N_2 did not stop at the stage of the hydradizo(2-) form, but proceeded further to form NH_3 and NH_4^+. Thus, base distillation of the reaction mixture was carried out to liberate NH_3. Actually, when the reaction mixture of **1** and 10 equiv of **2** at 55 °C for 24 h was extracted with an excess of water instead of base distillation, the presence of NH_3 in 50% yield based on the W atom was observed in the water extract. As expected, treatment of **1** with 10 equiv of thiophenol (PhSH) or an excess of H_2S under the same reaction conditions led to evolution of H_2 gas without the formation of NH_3,[11] whereas in the case of a more acidic thiol (p-$CF_3C_6F_4SH$), NH_3 was obtained in a low yield (9% total yield).

In contrast to the above iridium complex, the corresponding rhodium complex, $[Cp^*Rh(\mu\text{-}SH)_3RhCp^*]Cl$[10c] (**3**), afforded a small amount of NH_3 (7% total yield) under the same reaction conditions. Furthermore, the iron complex $[P_3Fe(\mu\text{-}SH)_3FeP_3]$-

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[11] An excess of methanol (pK_a 15.5) reacts with **1** at 50 °C to form NH_3 in good yield.[20] Both PhSH (pK_a 6.6) and H_2S (pK_a 7.0) are assumed to have enough acidity to protonate the coordinated N_2 in the complex **7**; however, protonation did not occur.

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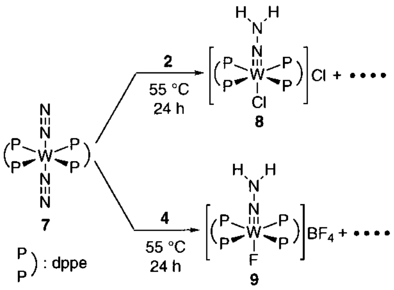
Table 1. Protonation of Coordinated Dinitrogen on Tungsten with Sulfido-Bridged Dinuclear Complexes to Produce Ammonia[a]

complex	temp (°C)	time (h)	yield of NH_3 (%)[b] free[c]	basic[d]	total	complex	temp (°C)	time (h)	yield of NH_3 (%)[b] free[c]	basic[d]	total
2	55	24	3	75	78	**3**	55	24	3	4	7
2	55	60	0	91	91	**4**	55	24	2	36	38
2	30	24	2	26	28	**5**	55	24	0	6	6
2	55	24			50[e]	**6**	55	24	2	7	9

[a] All of the reactions were carried out in dichloroethane−benzene using 0.10 mmol of **1** and 1.00 mmol of complex. [b] Yield of NH_3 was based on the W atom. [c] Free yield was before base distillation of the reaction mixture. [d] Basic yield was after base distillation to fully liberate NH_3. [e] This yield of NH_3 was observed in the water extract of the reaction mixture (see text).

Scheme 2



BF_4[12] (**4**; P_3 = bis(2-diphenylphosphinoethyl)phenylphosphine) was employed as a closer model component of nitrogenase because μ-SH moieties bound to *the iron atoms* in nitrogenase are considered to mediate proton transfer to coordinated N_2 (*vide supra*). In this reaction, NH_3 was formed in 38% total yield. However, metal products could not be characterized. In the present model reactions, we consider that proton was transferred through the intermolecular interaction between the μ-SH ligand in the dinuclear complexes and the coordinated N_2 on W atom (*vide infra*).

On the other hand, the neutral hydrosulfido-bridged diiridium complex, [Cp*IrCl(μ-SH)$_2$IrClCp*][10b,c] (**5**), afforded NH_3 in a lower yield than the above cationic hydrosulfido-bridged complex **2**.[13] This shows that the μ-SH ligand in the cationic complex is more acidic than that in the neutral complex. A heterodinuclear complex, [Cp*RuCl(μ-SH)$_2$TiCp$_2$][14] (**6**), also gave a low yield of NH_3.

The reaction of *trans*-[W(N$_2$)$_2$(dppe)$_2$] (**7**) with 2 equiv of **2** or **4** under a nitrogen atmosphere in dichloroethane−benzene at 55 °C for 24 h gave the hydradizo(2-) complexes *trans*-[WCl(NNH$_2$)(dppe)$_2$]Cl (**8**) and *trans*-[WF(NNH$_2$)(dppe)$_2$]BF$_4$ (**9**) in 60% and 80% NMR yields, respectively (Scheme 2).[15] The same hydrazido(2-) complexes were previously obtained from **7** by protonation with HCl or HBF_4.[5a,6a] Furthermore, the direct transfer of a proton from the μ-SH ligand in the dinuclear complex **4** to the coordinated N_2 in complex **1** was *preliminarily* confirmed by the experiment using the deuterated hydrosulfido complex [P$_3$Fe(μ-SD)$_3$FeP$_3$]BF$_4$ (**4′**); the deuterated hydrazido(2-) complex [WF(NND$_2$)(dppe)$_2$]$^+$ **9′** (ν_{ND} = 2399 cm^{-1}) and nondeuterated hydrazido(2-) complex **9** were obtained in 35 and 45% NMR yield, respectively, under the same reaction conditions.[16] These results provide direct evidence for protonation of the coordinated N_2 with the μ-SH ligand in these dinuclear complexes. Thus, the formation of NH_3 by the reaction of **1** with the above hydrosulfido-bridged complexes is also considered to proceed through hydrazido(2-) intermediates. These findings indicate that the μ-SH ligand[17] especially in the cationic dinuclear complexes is able to protonate the coordinated N_2 on W atom, in sharp contrast to RSH and H_2S.

Scheme 3

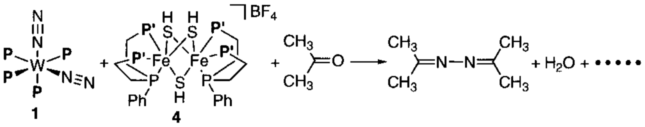


Table 2. Protonation of Coordinated Dinitrogen on Tungsten with Sulfido-Bridged Dinuclear Complexes to Produce Acetone Azine[a]

complex	temp (°C)	time (h)	acetone azine (%)[b]	complex	temp (°C)	time (h)	acetone azine (%)[b]
2	55	24	48	**4**	55	48	95
2	55	48	74	**5**	55	24	14
2	30	48	67	**6**	55	24	15
3	55	24	8	**10**	55	24	15

[a] All of the reactions were carried out in acetone−benzene using 0.10 mmol of **1** and 1.00 mmol of complex. [b] Yield of acetone azine was based on the W atom.

Interestingly, treatment of **1** in the presence of acetone with 10 equiv of **2** under nitrogen atmosphere in benzene at 55 °C for 24 h afforded acetone azine in 48% yield based on the W atom (Scheme 3). The typical results were shown in Table 2. In contrast to the formation of NH_3, **4** produced acetone azine in a yield higher than **2**. Other hydrosulfido-bridged dinuclear complexes such as **5**, **6**, and [Cp*RuCl(μ-SH)$_2$RuClCp*][10a] (**10**) afforded acetone azine in 14−15% yield under the same conditions. In the absence of the hydrosulfido-bridged dinuclear complexes, no acetone azine was formed. On the other hand, employment of dirhodium sulfido-bridged complexes such as [Cp*RhCl(μ-SH)$_2$RhClCp*],[10b] [(PPh$_3$)$_2$RhHCl(μ-SH)$_2$RhHCl(PPh$_3$)$_2$],[18] and [(triphos)RhH(μ-SH)$_2$RhH(triphos)](PF$_6$)$_2$[19] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) did not give rise to the formation of acetone azine. The formation of acetone azine in these reactions is considered to proceed through diazoalkane intermediates containing the W=N−N=CMe$_2$ moiety, which is formed by the condensation of a hydrazido(2-) intermediate with acetone. The mechanism is essentially the same as that proposed previously for the reaction of **1** with a methanol/acetone mixture.[20]

In summary, we have found that coordinated N_2 on the W atom can be protonated with the μ-SH ligand in dinuclear complexes to produce NH_3 and acetone azine under mild conditions. The cationic μ-SH dinuclear complexes **2** and **4** are the most effective for protonation of coordinated N_2. To our knowledge, this is the first example of proton transfer from metal SH complexes to coordinated N_2. Whether such proton transfer occurs in nitrogenase is still completely open to conjecture; however, this type of model system will provide valuable information about the mechanism of biological nitrogen fixation by nitrogenase.

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(13) The ^{1}H NMR spectrum of the reaction mixture showed the formation of the cubane cluster [(Cp*Ir)$_4$(μ-S)$_4$], which was previously obtained by the reaction of **5** and Et$_3$N.[10b,c]

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(15) The anion (chloride or fluoride) in the hydradizo(2-) complexes **8** and **9** came from the counteranion of the hydrosulfido complexes **2** and **4**.

(16) The relatively low yield of **9′** is considered to be due to the reaction of **7** with the nondeuterated hydrosulfido complex **4**, which was probably formed by the reaction of the deuterated hydrosulfido complex **4′** with adventitious water in the solvent.

(17) Since the μ-SH dinuclear complexes (**2**−**6**) are readily deprotonated by Et$_3$N, the pK_a values of these complexes are estimated to be far below the pK_a of Et$_3$NH$^+$ (10.8).

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