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Protonation of Coordinated N_2 on Tungsten with H_2 Mediated by Sulfido-Bridged Dinuclear Molybdenum Complexes[1]

Yoshiaki Nishibayashi,[†,‡] Issei Wakiji,[†] Kenji Hirata,[†] Mary Rakowski DuBois,*[,§] and Masanobu Hidai*[,†,⊥]

Department of Chemistry and Biotechnology, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, Colorado 80309-0215

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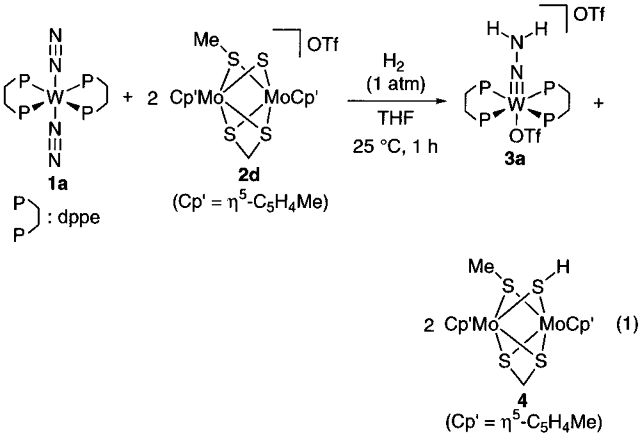
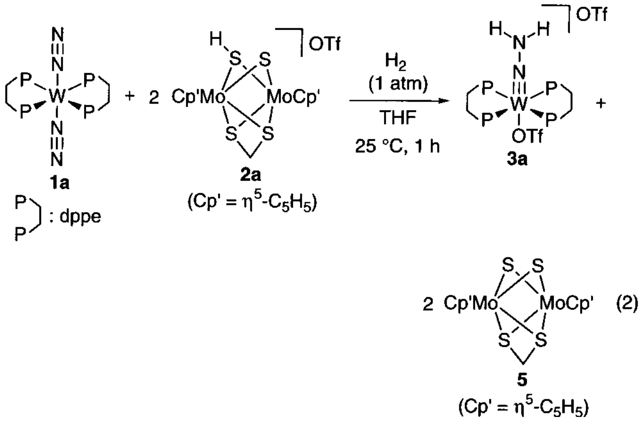
Introduction

During the course of our continuing study of the reactivities of coordinated N_2 in molybdenum and tungsten complexes of the type $[M(N_2)_2(L)_4]$ (M = Mo, W; L = tertiaryphosphine),[2] we have recently found that the coordinated N_2 on tungsten can be protonated with acidic ruthenium dihydrogen complexes to form NH_3 under mild conditions.[3] Furthermore, the coordinated N_2 is transformed into NH_3 by treatment with hydrosulfido-bridged dinuclear iridium and iron complexes, although organic thiols and H_2S are not effective for the reaction.[4] This indicates that a similar type of protonation might occur in biological nitrogen fixation, which is mediated by the bridging sulfur ligands in the FeMo cofactor.[5] An extension of our study has now led to the investigation of the reactions of the N_2 complexes with the sulfido-bridged dimolybdenum complexes $[Cp'Mo(\mu_2\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)MoCp']OTf$ (**2a**, Cp′ = η^5-C_5H_5, R = H; **2b**, Cp′ = η^5-C_5H_5, R = Me; **2c**, Cp′ = η^5-C_5H_4Me, R = H; **2d**, Cp′ = η^5-C_5H_4Me, R = Me; OTf = OSO_2CF_3) under H_2 because DuBois and co-workers previously reported that the C≡N triple bond in nitriles can be cleaved in the presence of **2a** under H_2 and complex **2d** induces the heterolytic cleavage of H_2 by reaction with pyridine under H_2.[6,7] The results are described here.

Results and Discussion

Treatment of *trans*-$[W(N_2)_2(dppe)_2]$ (**1a**; dppe = 1,2-bis(diphenylphosphino)ethane) with 2 equiv of $[(\eta^5\text{-}C_5H_4Me)Mo(\mu_2\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)Mo(\eta^5\text{-}C_5H_4Me)]OTf$ (**2d**) in THF at 25 °C for 1 h under 1 atm of H_2 produced the hydrazido(2−) complex *trans*-$[W(OTf)(NNH_2)(dppe)_2]OTf$ (**3a**) and $[(\eta^5\text{-}C_5H_4Me)Mo(\mu_2\text{-}S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SH)Mo(\eta^5\text{-}C_5H_4Me)]$ (**4**) in >99% and 69% NMR yields, respectively (eq 1). Under N_2, no reaction proceeded, and both **1a** and **2d** were recovered quantitatively. Hydrazido(2−) complex **3a** was previously obtained by protonation of **1a** with 2 equiv of trifluoromethanesulfonic acid (HOTf).[8] In the reaction of **1a** and **2d**, the heterolytic splitting of H_2 occurs on **2d**, where one H atom is used for the N−H bond formation at the coordinated N_2 on the W atom and the other H atom remains at the bridging-sulfido ligand. The formal oxidation state of the starting and product molybdenum complexes is +IV and +III, respectively, and the two electrons required for the reduction come from the H_2. Employment of **2b** in place of **2d** also gives rise to the formation of **3a** in high yield. On the other hand, when **1a** was treated with **2a** under H_2, **3a** and $[(\eta^5\text{-}C_5H_5)Mo(\mu_2\text{-}S_2CH_2)(\mu\text{-}S)_2Mo(\eta^5\text{-}C_5H_5)]$ (**5**) were obtained in >99% and 84% NMR yields, respectively (eq 2). The neutral molybdenum complex **5** is presumed to be formed from dehydrogenation of the initially formed complex $[(\eta^5\text{-}C_5H_5)Mo(\mu_2\text{-}S_2CH_2)(\mu\text{-}SH)_2Mo(\eta^5\text{-}C_5H_5)]$.[9]





[†] The University of Tokyo.

[‡] Present address: Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan.

[§] University of Colorado at Boulder.

[⊥] Present address: Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan.

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Table 1. Reaction of Coordinated N_2 on Tungsten and Sulfido-Bridged Dinuclear Molybdenum Complexes under H_2[a]

				yield of NH_3 (%)[b]		
run	W−N_2 complex	Mo complex	condition temp (°C)/time (h)	free[c]	in extract[d]	total
1	**1b**	**2a**	25/24 → 55/24	3	35	38[e]
2	**1b**	**2a**	25/120	4	30	34
3	**3b**[f]	**2a**	25/24 → 55/24	5	94	99
4	**1b**	**2b**	25/24 → 55/24	5	28	33
5	**1b**	**2c**	25/24 → 55/24	3	43	46
6	**1b**	**5**	25/24 → 55/24	5	12	17
7	**1b**	**6**	25/24 → 55/24	2	15	17
8	**1c**	**2a**	25/24 → 55/24	4	48	52[e]

[a] All of the reactions were carried out in THF using W−N_2 complex and 10 equiv of Mo complex under 1 atm of H_2 at 25 °C for 24 h and then at 55 °C for 24 h unless otherwise stated (see text). [b] Yield of NH_3 was based on the W atom. [c] Free NH_3 was observed in the reaction mixture. [d] Yield of NH_4^+ in the water extract of the reaction mixture. [e] Variation of ±8% between experiments. [f] **3b** was used in place of W−N_2 complex.

Interestingly, treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1b**) with 10 equiv of **2a** under 1 atm of H_2 in THF at 25 and then 55 °C for 24 h each resulted in the formation of NH_3 in 38% total yield based on the W atom, whereas reactions of **1a** under similar conditions did not produce NH_3. Free NH_3 in 3% yield was detected in the reaction mixture, and further NH_3 in 35% yield was observed as NH_4^+ in the water extract when the reaction mixture was extracted with an excess of water. The typical results are shown in Table 1. In the absence of H_2 or **2a**, no NH_3 was formed. When the reaction was performed at 25 °C for a much longer time, NH_3 was produced in moderate yield even at that temperature (Table 1, run 2). However, if the reaction was carried out at 55 °C, the formation of NH_3 was not observed. This is probably because **2a** reacts much more quickly with THF than with **1b** at that temperature to give a cationic complex with a 4-hydroxybutanethiolate ligand.[10] In all cases, only a trace amount of NH_2NH_2 was observed. When **1b** was treated with 2 equiv of **2a** at 25 °C for 1 h under H_2, the formation of the hydrazido(2−) complex *trans*-$[W(OTf)(NNH_2)(PMe_2Ph)_4]OTf$[3b] (**3b**) in 39% yield was revealed by NMR analysis of the reaction mixture. Furthermore, the reaction of **3b** with 10 equiv of **2a** under H_2 at 25 and then 55 °C for 24 h each produced NH_3 in 99% total yield (Table 1, run 3). These results indicate that the formation of NH_3 proceeds through the protonation of **3b** as an intermediate.

Reactions of **1b** with 10 equiv of other cationic sulfido-bridged dinuclear molybdenum complexes (**2b** and **2c**) under H_2 led to the formation of NH_3 in similar yields (Table 1, runs 4 and 5). However, in the case of neutral dinuclear molybdenum complexes such as **5** and $[(\eta^5\text{-}C_5H_5)Mo(\mu\text{-}SH)(\mu\text{-}S)]_2$ (**6**), NH_3 was obtained in lower yields (Table 1, runs 6 and 7).

The reaction of *trans*-$[W(N_2)_2(PMePh_2)_4]$ (**1c**) with 10 equiv of **2a** under the same conditions gave NH_3 in 52% yield (Table 1, run 8), which is almost the same as that from the reaction of **1b** with **2a** (vide supra). This is in sharp contrast to our previous observation that treatment of **1b** with 10 equiv of *trans*-$[RuCl(\eta^2\text{-}H_2)(dppe)_2]OTf$ at 55 °C under H_2 gives NH_3 in moderate yield while the similar reaction of **1c** affords NH_3 in very low yield.[3b]

In summary, we have found that the reactions of tungsten N_2 complexes and sulfido-bridged dinuclear molybdenum complexes under H_2 produce NH_3 under mild conditions. The reaction mechanism is not yet clear; however, it is noteworthy that sulfido-bridged dinuclear molybdenum complexes are able to induce heterolytic cleavage of H_2, leading to the N−H bond formation of coordinated N_2. Thus, heterolytic H_2 activation at a metal−sulfur site, i.e., $M{-}S + H_2 \rightarrow M(H^-){-}SH^+$, has been proposed to realize catalytic nitrogen fixation.[11]

Experimental Section

General Procedure. Preparation of complexes was performed under 1 atm of N_2 or Ar dried by passage through silica gel and P_2O_5. Reactions of N_2 complexes with sulfido-bridged dimolybdenum complexes were carried out under 1 atm of H_2 dried by passage through silica gel and P_2O_5. THF was freshly distilled over sodium benzophenone ketyl just before use. Unless otherwise noted, all manipulations were done by use of Schlenk techniques. NMR spectra were run on a JEOL JNM-LA-400 or a JEOL JNM-EX-270 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer. Absorption spectra were measured on a Shimadzu UV-2400PC. Tungsten N_2 complexes[12−14] (**1**) and sulfido-bridged dimolybdenum complexes[15,16] (**2**, **5**, **6**) were prepared according to literature procedures.

Reaction of *trans*-$[W(N_2)_2(dppe)_2]$ (1a) with Sulfido-Bridged Dinuclear Molybdenum Complexes (2) under H_2. A typical experimental procedure for the reaction of **1a** with 2 equiv of **2d** is as follows. In a 20 mL flask was placed **2d** (28.6 mg, 0.0436 mmol) under 1 atm of N_2. Dry THF (15 mL) was added, and then the solution was magnetically stirred at 25 °C for 5 min. After the N_2 atmosphere was replaced by 1 atm of H_2, **1a** (22.5 mg, 0.0217 mmol) was added portionwise. The reaction mixture was stirred at 25 °C for 1 h under 1 atm of H_2. The solvent was then removed under vacuum, and the residue was dissolved in THF-d_8 to measure the ^1H NMR spectrum. Ferrocene (10.1 mg, 0.0554 mmol) was added into the THF-d_8 solution as an internal reference. The NMR yield of the produced dimolybdenum complex (**4**) was determined by integration of the ^1H resonances against the ferrocene standard. However, the NMR yield of the produced hydrazido(2−) complex (**3a**) could not be determined in this solvent because of overlap of the ^1H resonances with those of impurities. Thus, the solvent was again evaporated under vacuum, and the residue was dissolved in $CDCl_3$ to determine the NMR yield of **3a** by integration of the ^1H resonances against the ferrocene standard. **4**:[17] ^1H NMR (THF-d_8) δ −1.35 (br s, 1H, SH), 1.52 (s, 3H, SMe), 2.00 (s, 6H, C_5H_4Me), 5.43 (br, 8H, C_5H_4Me), 5.79 (s, 2H, S_2CH_2); 69% NMR yield. **3a**:[8] ^1H NMR ($CDCl_3$) δ 2.87 (br s, 4H, CH_2), 3.00 (br s, 4H, CH_2), 5.01 (br s, 2H, NNH_2), 7.21−7.45 (m, 40H, Ph); >99% NMR yield; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.8 (s with ^{183}W satellites, J_{PW} = 320 Hz).

Formation of NH_3 in the Reactions of Dinitrogen Tungsten Complexes (1b, 1c) with Sulfido-Bridged Dinuclear Molybdenum Complexes (2) under H_2. A typical procedure for the reaction of **1b** with 10 equiv of **2a** under 1 atm of H_2 is as follows. In a 500 mL flask was placed **2a** (307 mg, 0.500 mmol) under 1 atm of N_2. Dry THF (20 mL) was added, and then the mixture was magnetically stirred at 25 °C for 5 min. After the N_2 atmosphere was replaced by 1 atm of H_2,

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1b (39.4 mg, 0.0497 mmol) was added portionwise. The reaction mixture was stirred at 25 and then 55 °C for 24 h each under 1 atm of H_2. The reaction mixture was evaporated under reduced pressure, and the distillate was trapped in dilute H_2SO_4 solution (1 N; 10 mL). The residue was extracted with H_2O (150 mL), and the aqueous extract was treated with activated charcoal and filtered through Celite. NH_3 and NH_2NH_2 present in the H_2SO_4 and the aqueous solution were quantitatively analyzed by using indophenol and *p*-(dimethylamino)-benzaldehyde reagents, respectively.[3b,18,19]

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