

Communications to the Editor

Catalytic Disproportionation and Reduction of Hydrazine by Sulfur-Ligated Molybdenum(IV) Complexes. Characterization of the Catalytic Precursor

$[(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_2\text{Cl}_2\text{Mo}(\mu\text{-S}_2)(\mu\text{-2-SC}_5\text{H}_3\text{NH-3-SiMe}_3)_2\text{MoCl}_2(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)]\cdot\text{thf}$

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While the role played by molybdenum in the reduction of dinitrogen by nitrogenases remains enigmatic,^{1,2} the coordination chemistry of molybdenum with sulfur-containing ligands may be relevant to this process since it is possible that at least one end of dinitrogen binds to a molybdenum center in an intermediate oxidation state.³ Synthetic and mechanistic studies of model complexes, which focus on low-oxidation-state, mononuclear molybdo-phosphine complexes of the type $[\text{M}(\text{N}_2)_2(\text{PR}_3)_4]$,⁴ have established that a single metal center is sufficient for stoichiometric reduction of N_2 to ammonia and that hydrazido(2-) complexes, $\text{M}=\text{NNH}_2$, are key intermediates. In contrast, relatively few studies of N-N bond activation by molybdenum species in high oxidation states,⁵ or with sulfur ligands, and/or of higher nuclearity have been described.

Although thiolate ligands may be most suitable for modeling the sulfido environment of the molybdenum center in nitrogenase, few examples of high-oxidation-state Mo-thiolate complexes capable of further substitution chemistry are known,^{6,8} with the notable exceptions of $[\text{Mo}(\text{SCMe}_3)_4]$ ⁶ and $[\text{Mo}(\text{SC}_6\text{H}_4\text{-2,4,6-Pr}^i_3)_4]$.⁷ As part of our continuing investigations of the chemistry of metal-thiolate complexes,⁹ we have described the chemistry of singly or multiply silylated 2-pyridinethiols. The silylated 2-pyridinethiol ligands 2-HSC₅H₃N-3-SiR₃ (R = Me, **1**; R = Prⁱ, **2**) and 2-HSC₅H₃N-6-SiMe₂Bu^t (**3**) react with Mo(IV) precursors such as $[\text{MoCl}_4(\text{CH}_3\text{CN})_2]$ to give mononuclear and binuclear complexes of the types $[\text{MoCl}_4(\text{SR})_2]$ (SR = 2-SC₅H₃NH-3-SiMe₃, **4**; 2-SC₅H₃NH-3-SiPrⁱ, **5**; and 2-SC₅H₃NH-6-SiMe₂Bu^t,

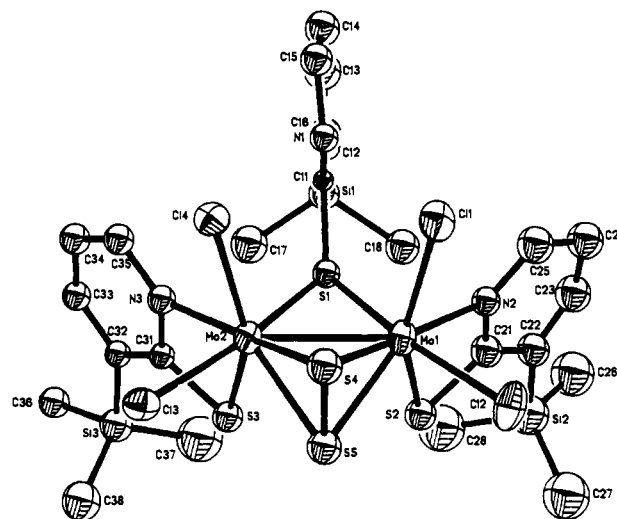


Figure 1. ORTEP view of the structure $[\text{Mo}_2\text{Cl}_4(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_2(\mu\text{-S}_2)(\mu\text{-2-SC}_5\text{H}_3\text{NH-3-SiMe}_3)]$.

6) and $[\text{Mo}_2(\text{SR})_3\text{Cl}_6]$ (SR = 2-SC₅H₃NH-3-SiMe₃, **7**; 2-SC₅H₃NH-6-SiMe₂Bu^t, **8**),⁹ where the ligand is present in the neutral pyridine-2(1*H*)-thione form with the nitrogen protonated.¹⁰ We now report that reactions of $[\text{MoCl}_5]$ with excess **1** result in reduction of the molybdenum to give the unusual binuclear complex $[\text{Mo}_2\text{Cl}_4(\mu\text{-S}_2)(\mu\text{-2-SC}_5\text{H}_3\text{NH-3-SiMe}_3)(2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3)_2]\cdot\text{thf}$ (**9**), which serves as a precursor for both catalytic disproportionation and reduction of hydrazine.

Complex **9** is produced in the reaction of $[\text{MoCl}_5]$ with 4 equiv of **1** in CH_2Cl_2 , requiring that **1** act as a reductant and source of S_2^{2-} , to give the bispyridyl sulfide $[(3\text{-Me}_3\text{Si-2-NC}_5\text{H}_3)_2\text{S}]$ ¹¹ as the major organic product. As shown in Figure 1, the structure of **9** consists of discrete binuclear molecules with the molybdenum centers bridged by a disulfide and a thione sulfur donor,¹¹ an unusual geometry for Mo(IV)-Mo(IV) binuclear complexes¹² but somewhat reminiscent of those of the tetrahydrothiophene complex $[\text{Mo}_2\text{Cl}_6(\text{C}_4\text{H}_8\text{S})_2(\mu\text{-S}_2)(\mu\text{-C}_4\text{H}_8\text{S})]$ (**10**)¹³ and of $(\text{NEt}_4)_2\text{-}[\text{Mo}_2\text{Cl}_6(\mu\text{-S}_2)(\mu\text{-Cl})_2]$ (**11**).¹⁴

In the absence of external reductant and proton source, complex **9** effects the catalytic disproportionation of hydrazine to ammonia and molecular nitrogen,¹⁵ as illustrated by the data summarized in Table I. At room temperature, a total of 1200 equiv of NH_3 /(equiv of dimer) was obtained over a 17-day period. The rate of ammonia evolution increased monotonically from 0.3 mol of NH_3 /(mol of **9**)h at -5°C to 2.4 mol of NH_3 /(mol of **9**)h at $+35^\circ\text{C}$. Dinitrogen was identified as the other nitrogenous product of this reaction, and in one example 95% of the nitrogen

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(15) Reactions were carried out in CH_2Cl_2 at room temperature under argon. The ammonia was quantified by the indophenol method¹⁶ and hydrazine using *p*-(dimethylamino)benzaldehyde.¹⁷ In one set of experiments (see Table I and supplementary material), N_2 evolution was measured by use of a Toepler pump and confirmed by mass spectroscopy/gas chromatography.

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Table I. Catalytic Ammonia Production under Conditions of Disproportionation (A) and Reduction (B)^a

complex	A: no external reductant ^b			B: Zn amalgam/lutidine-HCl added ^d		
	added N ₂ H ₄ , ^b equiv	NH ₃ yield, ^c equiv	conversion, ^e %	added N ₂ H ₄ , equiv	NH ₃ yield, ^d equiv	conversion, ^f %
9	12 (5)	15.20 (16)	95	12 (2)	20.6 (24) ^d	86
	36 (2)	43.20 (48)	90	36 (1)	61.2 (72)	83
	216 (2)	184.32 (288)	64	280 (2)	476.0 (560)	85
	1440 (1)	1232.00 (1920)	64	1200 (1)	2045.0 (2400)	85
4	12 (2)	14.80 (16)	93	180 (2)	315.2 (360)	88
	216 (1)	179.25 (288)	62	360 (2)	583.2 (720)	81
N ₂ H ₄	g	g	2	g	g	3

^aA complete table of all experiments is provided in the supplementary material. ^bNumber of experiments is in parentheses. ^cMaximum yield possible by disproportionation is in parentheses. ^dMaximum yield possible by reduction is in parentheses. ^eIn one set of experiments, the yields of all nitrogen-containing products were quantified: for 122 equiv of N₂H₄ added, 15.20 equiv of NH₃, 3.82 equiv of N₂, and a trace amount of N₂H₄ were observed; these results give a N balance of 95%. Using 95% ¹⁵N labeled hydrazine, a nearly quantitative amount of ¹⁵NH₃ and ¹⁵N₂ (91%) was recovered as determined by ¹⁵N NMR and by mass spectroscopy/gas chromatography. ^fFor 12 equiv of N₂H₄, 20.6 equiv of NH₃ and 1.3 equiv of N₂ were obtained, for a 97% nitrogen balance. ^gWith no complex present, traces of ammonia could be detected upon stirring CH₂Cl₂ solutions containing 0.05, 0.10, 0.20, and 0.50 mol of N₂H₄. A maximum conversion of 2% was observed after 7 days at room temperature. Addition of Zn amalgam and lutidine hydrochloride in the absence of complex did not significantly enhance ammonia concentrations. ^hThe rate of ammonia evolution at room temperature for **9** is 1.8 mol of NH₃/(mol of **9**)h, averaged over a 5-day period. ⁱThe rate of ammonia evolution upon addition of lutidine hydrochloride is 6.6 mol of NH₃/(mol of **9**)h, averaged over a 5-day period.

was accounted for. Furthermore, in the presence of zinc amalgam and 2,6-lutidine hydrochloride, enhanced levels of ammonia as well as increased rates of evolution are observed, features consistent with catalytic reduction.¹¹

The structurally related Mo(IV)-disulfido bridged binuclear complexes **10** and **11** were treated with hydrazine under conditions identical to those employed for **9** and were found to yield levels of ammonia slightly above background. On the other hand, the mononuclear complex **4** is effective in both the disproportionation and the reduction of hydrazine. However, **4** has been shown to yield binuclear species under reaction with hydrazine,⁹ a reaction which may be monitored by changes in the electronic spectrum of **4** upon addition of various amounts of hydrazine. Addition of ether to solutions of **4** which have been treated with more than 400 equiv of N₂H₄ and which remains active with respect to disproportionation results in the precipitation of black crystals of the active species **7**,⁹ an observation which supports the binuclear nature of the reactive intermediates. However, the electronic spectrum of **7**¹¹ is distinct from that of the reactive intermediate, whose identity has remained elusive.

Complex **9** is also observed to undergo a dramatic color change upon addition of hydrazine, from deep red to dark purple. The infrared spectrum of this solution is characterized by the disappearance of the 620-cm⁻¹ band associated with ν(S₂), while the electronic spectrum is identical to that of **4** in the presence of hydrazine, indicating a common reaction intermediate with no μ-S₂²⁻ linkage.

The importance of the 2(1H)-pyridinethione group in the overall chemistry of **9** is confirmed by methylation of the pyridine nitrogen, which yields [Mo₂Cl₄(μ-S₂)(2-SC₅H₃N-3-SiMe₃)₂(2-SC₅H₃NMe-3-SiMe₃)] (**13**),¹¹ a species which is unreactive toward hydrazine. However, since hydrazine may act as a Bronsted base and/or a redox reagent, as well as a ligand, complex **9** was treated with triethylamine in order to evaluate the consequences of base addition; the reaction was found to give a mixture of HNEt₃Cl, unidentified molybdenum-sulfido species, and a species analyzing for [Mo₂Cl₃(2-SC₅H₃N-3-SiMe₃)₃] (**12**).¹¹ Compound **12** was also obtained upon reaction of **9** with 1 equiv of hydrazine, with the formation of hydrazinium hydrochloride. Compound **12** is extremely unstable toward oxidation, producing [Mo₂O₃(2-SC₅H₃N-3-SiMe₃)₄] in the presence of trace amounts of O₂ or H₂O. The electronic spectrum of **12** is identical to that of the reactive species produced by hydrazine treatment of **9** and **4**. Furthermore, **12** catalyzes the disproportionation and reduction of hydrazine with quantitative results nearly identical to those of **9** and **4**. Since **12** is paramagnetic (μ_{eff} = 1.35μ_B/Mo), characterization by NMR spectroscopy was not feasible. Reactions of **12** with organohydrazines yield mononuclear species of the types [Mo(NNR₂)(2-SC₅H₃N-3-SiMe₃)₃]⁹ and [Mo(NNR₂)₂(2-SC₅H₃N-3-SiMe₃)₃]⁹. However, there is precedent for the reaction of unsymmetrically coordinated molybdenum dimers with organohydrazines to give binuclear molybdenum-

hydrazido species, as in the reaction of [Mo₂Cl₄(mbds)₃] (mbdsH₂ = PhCH(SH)SiMe₂CH(SH)Ph) with H₂NNPhMe to give [Mo₂Cl(mbds)₃(NNR₂)₂]⁺.¹⁸

The evidence suggests that the catalytic production of ammonia from hydrazine by **9** and **4** involves a common bimetallic intermediate of composition [Mo₂Cl₃(2-SC₅H₃N-3-SiMe₃)₃] (**12**), whose formation requires deprotonation of a ligand thione moiety with concomitant structural rearrangement involving loss of chloride groups and, in the case of **9**, the disulfido group. While a single metal center has been shown to be sufficient for the stoichiometric^{19,20} and catalytic reduction of hydrazine to ammonia,⁵ bimetallic activation of N-N bonds constitutes a persistent, albeit minor, theme in the literature of nitrogen fixation²¹⁻²³ and has received added impetus from the recently described bridged double cubane structures.^{24,25}

Although the active binuclear species **12** has not been unambiguously characterized, the results described establish that binuclear molybdenum complexes with a sulfur ligand environment and in a relatively high oxidation state are capable of N-N bond activation. The chemistry of N₂H_x and NH_y ligands with high-oxidation-state Mo-thiolate complexes may be extensive²⁶ and may define alternative chemical possibilities for abiological nitrogen fixation.

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Supplementary Material Available: Experimental procedures and tables of crystallographic parameters for the X-ray study of **9** and atomic positional parameters, bond lengths, and bond angles for **9** (13 pages); listing of observed and calculated structure factors for **9** (16 pages). Ordering information is given on any current masthead page.

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