Inorg. Chem. **2006**, *45*, 3164–3166

Inorganic Chemistry
Communication

Catalytic Reduction of Hydrazine to Ammonia by a Vanadium Thiolate Complex

Wei-Cheng Chu, Chi-Chin Wu, and Hua-Fen Hsu*

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 701

Received January 30, 2006

Vanadium(III) thiolate complexes, $[V(PS3'')(Cl)]^-$ [**1a**; PS3″ = $P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3{}^{3-}$] and $[V(PS3')(Cl)]^-$ [**1b**; PS3′ = $P(C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}S)_3{}^{3-}$], were synthesized and characterized. Complex **1a** serves as a precursor for the catalytic reduction of hydrazine to ammonia. The spectroscopic and electrochemical studies indicate that hydrazine is bound and activated in a V^{II} state.

Nitrogen fixation catalyzed by nitrogenases is an important process in biology.[1–3] Although the structure of molybdenum nitrogenase has been characterized by X-ray crystallography, how the enzyme catalyzes the reduction of dinitrogen and other substrates is still not fully understood.[4] To discern the mechanistic steps of nitrogen fixation carried by the enzyme, much effort has been made by researchers on synthetic metal complexes that activate N_2H_x molecules, substrates, and intermediates of nitrogenase.[5] Hydrazine is a substrate as well as an intermediate of nitrogenase.[6,7] However, reported synthetic analogues that catalyze the reduction of hydrazine to ammonia, the late stage of nitrogen fixation, are very limited.[8–14] They are mononuclear complexes MCp^*Me_3 core (M = Mo or W),[8,9] molybdenum thiolate complexes,[10,11] and MFe_3S_4 (M = Mo or V) cubanes.[12–14] The finding of vanadium nitrogenase prompts us and others to explore the reactivity of V compounds with substrates relevant to nitrogenase.[15,16] To continue our effort in this aspect, we have obtained a vanadium(III) thiolate complex, $[V(PS3'')(Cl)]^-$ [**1a**; PS3″ = $P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3{}^{3-}$], that servers as a precursor for the catalytic reduction of hydrazine. Notably, it is unprecedented that hydrazine reduction is catalyzed by a mononuclear V center, in particular, ligating with thiolate ligands and mimicking the sulfido environment of the V site in vanadium nitrogenase. We detail this chemistry herein.

The reaction of 1 equiv of $VCl_3(THF)_3$ in THF with 1 equiv of PS3″ in methanol generated a reddish-brown solution. The addition of $PPh_4{}^+$ in CH_2Cl_2 followed by layering pentane gave a crystalline solid of **1a** in 70% yield. An analogy of compound **1a**, $[V(PS3')(Cl)]^-$ [**1b**; PS3′ = $P(C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}S)_3{}^{3-}$], was obtained under a similar reaction using the PS3′ ligand. The structures of **1a** and **1b** characterized by X-ray crystallography are similar, and their ORTEP pictures are shown in Figure 1. Each structure embraces a five-coordinate V center with a trigonal-bipyramidal geometry in which the V center coordinates to a P atom, three thiolate groups, and a chloride trans to the P donor. The average V−S bond distances of 2.319(6) and 2.318(3) Å

---

* To whom correspondence should be addressed. E-mail: konopka@mail.ncku.edu.tw.

(1) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965.
(2) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983.
(3) Eady, R. R. *Chem. Rev.* **1996**, *96*, 3013.
(4) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696.
(5) (a) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. In particular, for V complexes that activate N_2H_x: (b) Ferguson, R.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 396. (c) Edema, J. J. H.; Meetsma, A.; Gambarotta, S. *J. Am. Chem. Soc.* **1989**, *111*, 6878. (d) Song, J.-I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927. (e) Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2004. (f) Leigh, G. J.; Prieto-Alcon, R.; Sanders, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, *14*, 921. (g) Gailus, H.; Woitha, G.; Rehder, D. *J. Chem. Soc., Dalton Trans.* **1994**, 3471. (h) Ferguson, R.; Solari, E.; Floriani, C.; Osella, D.; Ravera, M.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1997**, *119*, 10104. (i) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke, F. G. N. *J. Am. Chem. Soc.* **1999**, *121*, 10444. (j) Hao, S.; Berno, P.; Minhas, R. K.; Gambarotta, S. *Inorg. Chim. Acta* **1996**, *244*, 37. (k) Desmangles, N.; Jenkins, H.; Ruppa, K. B.; Gambarotta, S. *Inorg. Chim. Acta* **1996**, *250*, 1. (l) Vidyaratne, I.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Inorg. Chem.* **2005**, *44*, 1187.
(6) Thorneley, R. N. F.; Eady, R. E.; Lowe, D. J. *Nature* **1978**, *272*, 557.
(7) Barney, B. M.; Yang, T.-C.; Igarashi, R. Y.; Dos Santos, P. C.; Laryukhin, M.; Lee, H.-I.; Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C. *J. Am. Chem. Soc.* **2005**, *127*, 14960.
(8) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725.
(9) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760.
(10) Block, E.; Ofori-Okai, G.; Kang, H.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 758.
(11) Hitchcock, P. B.; Hughes, D. L.; Maguire, M. J.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 4747.
(12) Coucouvanis, D.; Mosier, P. E.; Demadis, K. D.; Patton, S.; Malinak, S. M.; Kim, C. G.; Tyson, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 12193.
(13) Demadis, K. D.; Malinak, S. M.; Coucouvanis, D. *Inorg. Chem.* **1996**, *35*, 4038.
(14) Malinak, S. M.; Demadis, K. D.; Coucouvanis, D. *J. Am. Chem. Soc.* **1995**, *117*, 3126.
(15) Eady, R. R. *Coord. Chem. Rev.* **2003**, *237*, 23.
(16) (a) Hsu, H.-F.; Chu, W.-C.; Hung, C.-H.; Liao, J.-H. *Inorg. Chem.* **2003**, *42*, 7369. (b) Davies, S. C.; Hughes, D. L.; Janes, Z.; Jerzykiewicz, L. B.; Richards, R. L.; Sanders, J. R.; Silverstone, J. E.; Sobota, P. *Inorg. Chem.* **2000**, *39*, 3485. (c) Crans, D. C.; Smee, J. J.; Gaidamauskas, E.; Yang, L. *Chem. Rev.* **2004**, *104*, 849.

10.1021/ic060171q CCC: $33.50

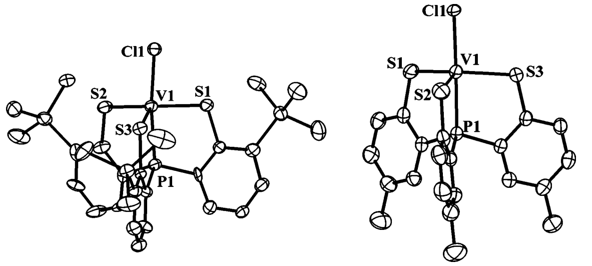

Figure 1. Thermal ellipsoid plots (35% probability) of the anions of **1a** (left) and **1b** (right). The H atoms and countercations have been omitted for clarity. Selected bond lengths [Å] and angles [deg] for **1a**: V1−S1 2.314(2), V1−S2 2.318(2),V1−S3 2.324(2), V1−Cl1 2.325(2), V1−P1 2.367(2), S2−V1−S1 116.46(8), S2−V1−S3 115.75(8), S1−V1−S3 122.48(8), S2−V1−Cl1 102.74(8), S1−V1−Cl1 92.55(7), S3−V1−Cl1 98.10(7), S2−V1−P1 82.57(7), S1−V1−P1 82.19(7), S3−V1−P1 82.18(7), Cl1−V1−P1 173.84(8). For **1b**: V1−S1 2.315(1), V1−S2 2.317(1), V1−S3 2.322(1), V1−Cl1 2.375(1), V1−P1 2.379(1), S1−V1−S2 118.31(5), S1−V1−S3 118.05(5), S2−V1−S3 119.09(5), S1−V1−Cl1 96.71(4), S2−V1−Cl1 96.50(4), S3−V1−Cl1 98.19(4), S1−V1−P1 82.87(4), S2−V1−P1 82.82(4), S3−V1−P1 82.90(4), Cl1−V1−P1 178.90(4).

found in **1a** and **1b**, respectively, are similar to those found in five-coordinate vanadium(III) thiolate complexes.[16a,b]

Importantly, compound **1a** catalyzes the reduction of N_2H_4 to NH_3 in CH_3CN with the presence of a reducing agent and a proton source, cobaltocene [$Co(Cp)_2$] and 2,6-lutidinium chloride (2,6-Lut•HCl), respectively (eq 1).[17] A total

$$N_2H_4 + 2e^- + 2H^+ \rightarrow 2NH_3 \qquad (1)$$

of 5 equiv of N_2H_4 can be reduced catalytically with a nearly quantitative yield (90%) after 48 h (Table S1 in the Supporting Information). In the absence of an external proton source and a reducing agent, the reaction of **1a** and N_2H_4 does not produce ammonia, indicating that **1a** does not assist the disproportionation of N_2H_4 (eq 2).

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad (2)$$

The reactions with various ratios of hydrazine to **1a** in CH_3CN at ambient temperature and pressure were investigated for the reaction time of 24 h, as shown in Table 1. Accordingly, a high yield of ammonia was generated when less than 5 equiv of N_2H_4 was attempted to be reduced. However, the yield was decreased in the reactions that attempted to reduce more than 5 equiv of N_2H_4.

The low conversion yield for reducing more equivalents of N_2H_4 is mainly attributed to the formation of [V(PS3″)(N_2H_4)$_3$] (**2**), a catalytically inactive compound. Compound **2**, reported previously, was obtained in 65% yield from the reaction of **1a** with 10 equiv of N_2H_4.[16a] However, **2** does not produce ammonia with the addition of $Co(Cp)_2$ and 2,6-Lut•HCl, implying that **2** is not a substrate-bound intermediate in the catalytic cycle of hydrazine reduction. This result is consistent with the electrochemical studies of **2**. The cyclic voltammogram (CV) of **2** in CH_3CN does not show any reduction wave in the range of −1.0 to −2.2 V [vs $Fe(Cp)_2/Fe(Cp)_2^+$]. The CV of cobaltocene measured at the same condition displays a redox potential corresponding to a $Co(Cp)_2/Co(Cp)_2^+$ couple at −1.33 V [vs $Fe(Cp)_2/Fe(Cp)_2^+$], indicating that $Co(Cp)_2$ is not a sufficient reducing agent to convert **2** to its reduced form.

Table 1. Catalytic Reduction of Hydrazine to Ammonia[a]

complex	added N_2H_4,[b] equiv	NH_3 yield, equiv	convn,[c] %
1a	1 (2)	2.0	100(0)
	3 (3)	5.5	92(2)
	5 (3)[d]	8.1	81(1)
	7 (3)	8.2	59(2)
	10 (3)	8.5	42(1)
	10 (2)[e]	NR[f]	NR
1b	3 (2)	NR[f]	NR

[a] The reaction time is 24 h. See the Supporting Information for reaction details and a complete table (Table S2). The indophenol method was used for ammonia analysis (ref 18). [b] The number of experiments is in parentheses. [c] The range (±) is shown in parentheses. [d] To ensure a N-atom balance, analyses for N_2H_4 were carried out after the reactions. A total of 0.91 and 0.85 equiv of N_2H_4 were detected for two experiments. The results gave a N-atom balance of approximately 95%. The PDMAB method was used for N_2H_4 analysis (ref 19). [e] Without $Co(Cp)_2$ and Lut•HCl present. [f] No ammonia is detected above the background level.

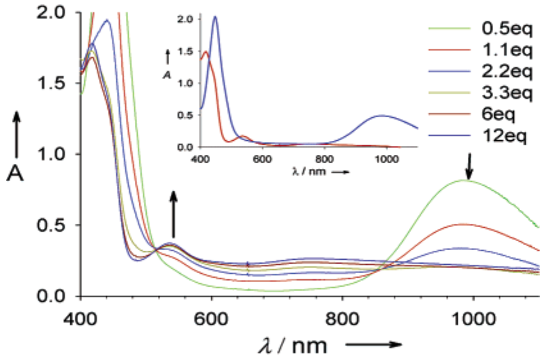

Figure 2. Variation in UV/vis/NIR spectra of **1a** in CH_2Cl_2 (7.68 × 10^{-4} M) with the addition of various equivalents of N_2H_4. Inset: UV/vis/NIR spectra of **1a** (4.61 × 10^{-4} M) in CH_2Cl_2 (blue line) and **2** (6.50 × 10^{-4} M) in CH_2Cl_2 (red line).

During speculation about hydrazine-bound intermediates in the catalytic cycle, titration of **1a** with N_2H_4 in CH_2Cl_2 at ambient temperature was monitored by UV/vis/NIR absorption spectroscopy, as shown in Figure 2.[20] Upon the addition of increasing amounts of N_2H_4, the characteristic band of **1a** at 992 nm gradually decreased while absorption increased at 537 nm, a feature of **2**. The conversion was marked by two isosbestic points, 515 and 860 nm, which strongly suggests that **2** is produced directly from **1a** and no other hydrazine-bound adducts such as [V(PS3″)(N_2H_4)] and [V(PS3″)(N_2H_4)$_2$] are formed in the reaction mixture. Thus, in the catalytic cycle of hydrazine reduction by **1a**, a substrate-binding species is at a V^{II} state rather than a V^{III} state. This leads to a possible reaction pathway in which **1a** is reduced to a V^{II} species prior to hydrazine binding.

---

(17) The following experiments without the addition of **1a** in CH_3CN at ambient temperature were carried out by Coucouvanis' laboratory: (a) the reaction of N_2H_4, $Co(Cp)_2$, and Lut•HCl and (b) the reaction of $Co(Cp)_2$ and Lut•HCl (ref 14). None of these reactions generated ammonia, ruling out possible ammonia production without the presence of **1a**.

(18) Chaney, A. L.; Marbach, E. P. *Clin. Chem. (Winston-Salem, N.C.)* **1962**, *8*, 130.

(19) Watt, G. W. *Anal. Chem.* **1952**, *24*, 2006.

(20) The titration was performed in CH_2Cl_2 instead of CH_3CN because of the insolubility of **2** in CH_3CN.

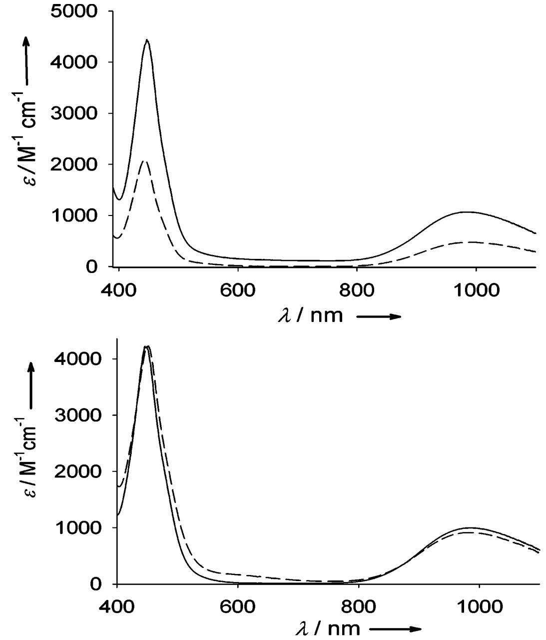

Figure 3. UV/vis/NIR spectra of **1a** (top) and **1b** (bottom) in CH_2Cl_2 (solid line) and CH_3CN (dashed line).

However, the CV of **1a** measured in CH_2Cl_2 displays an irreversible reduction wave at −2.48 V [vs Fe(Cp)$_2$/Fe(Cp)$_2^+$], much lower than the redox potential of Co(Cp)$_2$ measured at the same condition, which indicates that the reducing power of Co(Cp)$_2$ is not strong enough to reduce **1a** to a V^{II} state (Figure S1 in the Supporting Information). In contrast, when the CV of **1a** is performed in CH_3CN, the reduction wave shifted dramatically to −1.34 V. Likely, this is caused by the replacement of a bound chloride ion by a CH_3CN molecule, leading to the formation of [V(PS3″)(CH_3CN)]. Therefore, the reducing power of Co(Cp)$_2$ is strong enough to reduce [V(PS3″)(CH_3CN)] to a V^{II} species. The replacement of a bound chloride in **1a** by CH_3CN while dissolving **1a** in CH_3CN was confirmed by the UV/vis/NIR spectra, as shown in Figure 3. The spectra of **1a** taken in CH_2Cl_2 and CH_3CN display similar patterns with very different extinction coefficients. Indeed, the catalytic reaction carried out in CH_2Cl_2 rather than in CH_3CN produced no ammonia, consistent with the findings above.

The catalytic reductions of hydrazine by **1b** were also investigated in parallel (Table 1). Interestingly, no reaction yielded ammonia above the background level. This finding can be rationalized by the reduction wave of **1b** in CH_3CN appearing at −2.18 V [vs Fe(Cp)$_2$/Fe(Cp)$_2^+$], much lower than that of Co(Cp)$_2$ but similar to that of **1a** in CH_2Cl_2 (Figure S1 in the Supporting Information). This implies that the CH_3CN molecule does not replace the bound chloride ion in **1b** while dissolving **1b** in CH_3CN. This finding is also supported by the UV/vis/NIR spectra of **1b** taken in CH_2Cl_2 and CH_3CN that display almost identical absorption bands (Figure 3). The different reactivity of **1a** and **1b** toward the CH_3CN molecule is likely related to more electron-donating substituents in the PS″ ligand than in the PS′ ligand; electron donation to the V center would then facilitate the replacement of a bound anionic chloride by a neutral CH_3CN ligand. A reported $V^{III}N_2H_4$ compound, [V(NS3)(N_2H_4)] [NS3 = N(CH_2CH_2S)$_3^{3-}$], also does not carry the reduction of hydrazine with the external electron and proton sources.[16b] Failure to access a V^{II} oxidation state for **1b** and [V(NS3)(N_2H_4)] appears to be an explanation why these two compounds are catalytically inactive for hydrazine reduction.

In summary, we have isolated and characterized a vanadium(III) thiolate complex, **1a**, that servers as a precursor for the reduction of hydrazine catalytically. On the basis of spectroscopic and electrochemical studies, we propose that the initial step of the reaction involves the replacement of the bound Cl^- ion in **1a** by the solvent molecule, CH_3CN. Subsequently, [V(PS3″)(CH_3CN)] is reduced to a V^{II} species that binds and activates N_2H_4. Importantly, the vanadium thiolate complex shows reactivity in the N−N bond cleavage of hydrazine, an intermediate of nitrogen fixation, emphasizing the role of the V site in vanadium nitrogenase, which might be involved in the catalytic pathway of the late stage of nitrogen fixation. A further investigation of the reaction mechanism is in progress.

Acknowledgment. This work is supported by a grant from the National Science Council in Taiwan (Grant NSC 94-2113-M-006-013). We thank Prof. Ju-Hsiou Liao at National Chung Cheng University and Ting-Shen Kuo at National Taiwan Normal University for crystallographic structural determination.

Supporting Information Available: General consideration, physical methods, syntheses for complexes **1a** and **1b**, crystallographic determination and data for **1a** and **1b**, experiments for catalytic reactions, complete tables for catalytic reactions (Tables S1 and S2), cyclic voltammograms (Figure S1), and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060171Q