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Molybdenum-Catalyzed Transformation of Molecular Dinitrogen into Silylamine: Experimental and DFT Study on the Remarkable Role of Ferrocenyldiphosphine Ligands

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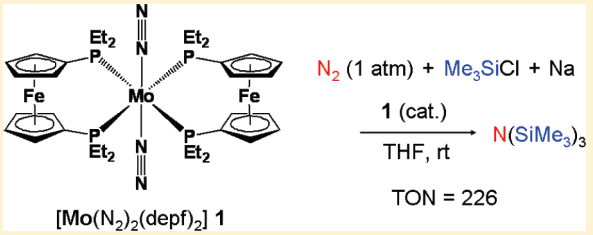
Supporting Information

ABSTRACT: A molybdenum−dinitrogen complex bearing two ancillary ferrocenyldiphosphine ligands, *trans*-$[Mo(N_2)_2(depf)_2]$ (depf = 1,1′-bis(diethylphosphino)ferrocene), catalyzes the conversion of molecular dinitrogen (N_2) into silylamine ($N(SiMe_3)_3$), which can be readily converted into NH_3 by acid treatment. The conversion has been achieved in the presence of Me_3SiCl and Na at room temperature with a turnover number (TON) of 226 for the $N(SiMe_3)_3$ generation for 200 h. This TON is significantly improved relative to those ever reported by Hidai's group for mononuclear molybdenum complexes having monophosphine coligands [*J. Am. Chem. Soc.* **1989**, *111*, 1939]. Density functional theory (DFT) calculations have been performed to figure out the mechanism of the catalytic N_2 conversion. On the basis of some pieces of experimental information, $SiMe_3$ radical is assumed to serve as an active species in the catalytic cycle. Calculated results also support that $SiMe_3$ radical is capable of working as an active species. The formation of five-coordinate intermediates, in which one of the N_2 ligands or one of the Mo−P bonds is dissociated, is essential in an early stage of the N_2 conversion. The $SiMe_3$ addition to a "hydrazido(2−)" intermediate having the $NN(SiMe_3)_2$ group will give a "hydrazido(1−)" intermediate having the $(Me_3Si)NN(SiMe_3)_2$ group rather than a pair of a nitrido (≡N) intermediate and $N(SiMe_3)_3$. The $N(SiMe_3)_3$ generation would not occur at the Mo center but proceed after the $(Me_3Si)NN(SiMe_3)_2$ group is released from the Mo center. The flexibility of the Mo−P bond between Mo and depf would play a vital role in the high catalysis of the Mo−Fe complex.



INTRODUCTION

Nitrogen fixation under ambient reaction conditions is one of the most important and challenging topics in chemistry.[1] Molecular dinitrogen (N_2) is chemically inert due to its extremely strong, nonpolar triple bond (225 kcal/mol) as well as the large HOMO−LUMO gap. Industrial nitrogen fixation typified by the Haber−Bosch process requires drastic reaction conditions of high pressures and high temperatures. Since the discovery of the first transition metal−N_2 complex $[Ru(N_2)(NH_3)_5]^{2+}$ by Allen and Senoff in 1965,[2] a great deal of effort has been devoted to the development of artificial nitrogen fixation systems that are capable of working under mild reaction conditions. Nowadays, a great number of well-defined N_2 complexes are known for almost all d-block transition metals as well as some f-block metals, and a lot of studies have been reported so far on stoichiometric transformation of their coordinated N_2 into ammonia (NH_3) and hydrazine (NH_2NH_2).[3−14] In 1975, for example, Chatt and co-workers found the formation of NH_3 by protonolysis of tungsten−N_2 and molybdenum−N_2 complexes $[M(N_2)_2(PR_3)_4]$ (M = Mo, W).[15] In sharp contrast to such stoichiometric reactivity of transition-metal−N_2 complexes, there are only a few examples of the catalytic transformation of N_2 into NH_3 and/or its NH_3 equivalent using transition metal complexes under mild reaction conditions.[16] In 1972, Shiina discovered the metal-chloride-catalyzed reductive transformation of N_2 into tris(trimethylsilyl)amine ($N(SiMe_3)_3$), which can be readily converted into NH_3 by acid treatment, in the presence of Me_3SiCl and lithium.[17] The turnover number (TON) of $N(SiMe_3)_3$ generation was up to 5.4 ($CrCl_3$). Hidai, Mizobe, and co-workers reported in 1989 a more effective method for $N(SiMe_3)_3$ generation using Me_3SiCl and sodium together with molybdenum−N_2 complexes such as $[Mo(N_2)_2(PMe_2Ph)_4]$ as a catalyst.[18] In their reaction system, the TON reached 24 based on the Mo atom. The mechanism of this catalytic reaction still remains to be elucidated although they proposed a mechanism involving a silyldiazenido intermediate formed by the attack of $SiMe_3$ radical on the N_2 ligand. Recently, Yandulov and Schrock reported the direct conversion of N_2 into NH_3 using a molybdenum−N_2 complex bearing an ancillary triamidoamine ligand.[19] They adopted a pair of proton and electron

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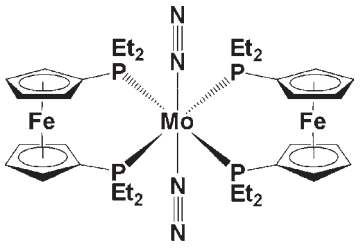
donors, lutidinium and decamethylchromocene, for the nitrogen fixation and proposed a catalytic mechanism containing successive hydrogenation of N_2 through alternating steps of protonation and reduction. The hydrogenation of a Mo−NNH_2 intermediate gives a nitrido (≡N) intermediate and the first molecule of NH_3, and then the nitrido ligand on Mo is converted into the second molecule of NH_3. At present, the validity of this mechanism is strongly supported by the isolation and observation of a large part of reactive intermediates as well as intensive theoretical studies on the catalytic cycle.[20−24] Unfortunately, the TON for the NH_3 generation was not very high (up to 8 based on the Mo atom).[25]

Quite recently, some of us have reported the synthesis and the stoichiometric reactivity of molybdenum−N_2 and tungsten−N_2 complexes bearing ferrocenyldiphosphines as auxiliary ligands, *trans*-[$M(N_2)_2$(depf)$_2$] (M = Mo (**1a**), W (**2a**); depf = 1,1′-bis(diethylphosphino)ferrocene), where the electron transfer process from the ferrocene moiety to the tungsten or molybdenum center may be expected to assist the reduction of the coordinated N_2 into NH_3.[26] During the continuous study on the development of novel nitrogen fixation system under mild reaction conditions,[27] a more efficient catalytic nitrogen fixation system was found by using **1a** as a catalyst. Dinitrogen under an atmospheric pressure was catalytically converted into $N(SiMe_3)_3$ in the presence of Me_3SiCl and sodium in quite a high TON.



trans-[$M(N_2)_2$(depf)$_2$]
M = Mo (**1a**), W (**2a**)

An intriguing subject is to elucidate how the coordinated N_2 is converted in this multimetallic system and how the depf ligands enhanced the catalysis for the conversion of N_2 into $N(SiMe_3)_3$. For the present reaction system, unfortunately, we have not obtained experimental information that can be directly associated with the determination of the catalytic mechanism. Computational quantum chemistry will provide a valuable insight into our understanding. Actually, some of us have computationally revealed the mechanisms on the activation and triple-bond cleavage of N_2 by a cubane-type $RuIr_3S_4$ cluster[28] as well as a hydride-bridged diniobium complex.[29] In this Article, we describe typical results of the catalytic conversion of N_2 into $N(SiMe_3)_3$ using **1a** as a catalyst and propose a possible reaction pathway by quantum chemical calculations.

RESULTS AND DISCUSSION

Catalytic Conversion of N_2 into $N(SiMe_3)_3$ by 1a. Typical experimental results are summarized in Table 1 for the conversion of N_2 into $N(SiMe_3)_3$ by using **1a** as a catalyst. Details are described in the Supporting Information. Treatment of Na (60 mmol) and Me_3SiCl (60 mmol) in the presence of a catalytic amount of **1a** (0.015 mmol) in THF (tetrahydrofuran; 40 mL) under an atmospheric pressure of N_2 at room temperature for 20 h gave 1.35 mmol of $N(SiMe_3)_3$ together with some side products such as $Me_3SiSiMe_3$, $Me_3Si(CH_2)_4OSiMe_3$, and $^nBuOSiMe_3$ (eq 1; Table 1, run 1). The generated $N(SiMe_3)_3$ was isolated from the reaction mixture and confirmed by ^1H and ^{13}C NMR and MS.

$$\underset{(1\ \text{atm})}{N_2} + \underset{(60\ \text{mmol})}{\text{reductant}} + \underset{(60\ \text{mmol})}{Me_3SiCl} \xrightarrow[\text{THF, rt}]{\text{catalyst (0.015 mmol)}} N(SiMe_3)_3 \quad (1)$$

The amounts of $N(SiMe_3)_3$ and other side-products were determined by GLC analysis. The TON for the formation of $N(SiMe_3)_3$ was 90 based on the Mo atom of **1a**. A longer reaction time (100 h) increased the amount of $N(SiMe_3)_3$ up to 1.77 mmol, corresponding to a TON of 118 (Table 1, run 2). In the reaction with Li as a reductant in place of Na (Table 1, run 3) for 100 h, a smaller amount of $N(SiMe_3)_3$ (0.56 mmol, TON = 37) was formed together with a larger amount of $Me_3SiSiMe_3$ (16.53 mmol). The reaction in a more dilute solution (60 mL of THF) yielded a larger amount of $N(SiMe_3)_3$ (2.25 mmol, TON = 150; Table 1, run 4) than the result of run 2 of Table 1. The TON reached 184 after 150 h, and Me_3SiCl was confirmed to be depleted in the reaction solution (Table 1, run 5). Here, we considered that the presence of more Na and Me_3SiCl may produce an extra amount of $N(SiMe_3)_3$ from the reaction mixture

Table 1. Reactions Using Reductant (60 mmol) and Me_3SiCl (60 mmol) Were Carried Out in the Presence of a Catalyst (0.015 mmol) under Atmospheric Pressure of N_2 at Room Temperature in THF

run	catalyst	reductant	THF (mL)	time (h)	amount of $N(SiMe_3)_3$ (mmol)[a]	TON[b]
1	**1a**	Na	40	20	1.35	90
2	**1a**	Na	40	100	1.77	118
3	**1a**	Li	40	100	0.55	37
4	**1a**	Na	60	100	2.25	150
5[c]	**1a**	Na	60	200	3.39	226
6	**3**	Na	40	20	0.48	32
7	**1b**	Na	40	20	0.81	54
8	**4**	Na	40	20	0.01	<1
9	**2a**	Na	40	20	0.90	60
10	**5**	Na	40	20	0.24	16
11	**6**	Na	40	20	0.18	12
12	**7**	Na	40	20	0.04	3
13	**8**	Na	40	20	0.66	44

[a] Determined by GLC. [b] TON = $N(SiMe_3)_3$/catalyst. [c] Another THF solution (60 mL) of Me_3SiCl (60 mmol) and Na (60 mmol) was added after 100 h.

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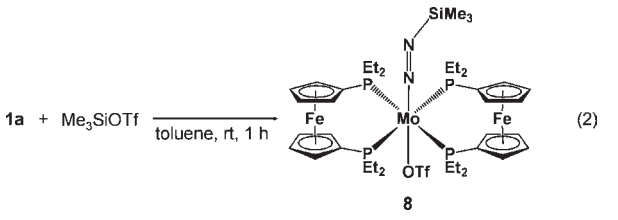
when the catalytic ability of **1a** is still alive at this stage. In fact, addition of Na (60 mmol) and Me_3SiCl (60 mmol) to the reaction solution after 100 h produced an extra amount of $N(SiMe_3)_3$ from the solution used in reaction mixture. The total amount of $N(SiMe_3)_3$ was finally measured to be 3.39 mmol with a TON of 226 (Table 1, run 5). Both N_2 gas and **1a** were confirmed to be indispensable for the formation of $N(SiMe_3)_3$ (see the Supporting Information).

Under the reaction conditions similar to run 1 in Table 1, replacement of **1a** with *trans*-$[Mo(N_2)_2(depf)(PMePh_2)]$ (**1b**) and *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (**3**) decreased the TONs to 54 and 32, respectively (Table 1, runs 6 and 7). Previously, Hidai's group reported that *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**4**) did not work as a catalyst for the formation of $N(SiMe_3)_3$.[18] We also confirmed that **4** did not catalyze this reaction under the same reaction conditions (Table 1, run 8). Interestingly, the reaction in the presence of a catalytic amount of *trans*-$[W(N_2)_2(depf)_2]$ (**2a**) gave $N(SiMe_3)_3$, where the TON reached 60 (Table 1, run 9). In sharp contrast to the efficient catalysis of **1a** and **2a**, low catalysis was observed for molybdenum−N_2 and tungsten−N_2 complexes having other diphosphines as ancillary ligands such as *trans*-$[Mo(N_2)(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino) ethane; **5**), *trans*-$[Mo(N_2)_2(depe)_2]$ (depe = 1,2-bis(diethylphosphino)ethane; **6**), and *trans*-$[W(N_2)_2(depr)_2]$ (depr = 1,1′-bis-(diethylphosphino)ruthenocene; **7**). The TONs for the $N(SiMe_3)_3$ formation were measured to be 16 for **5**, 12 for **6**, and 3 for **7** (Table 1, runs 10−12). All the experimental results clearly show that the depf ligands in **1a** and **2a** are responsible for their efficient catalysis. Unfortunately, we were not able to detect any structurally defined complexes by NMR after the catalytic reaction. As a piece of experimental information leading to elucidation of the catalytic mechanism, it should be noted that $N(SiMe_3)_3$ was not observed at all when dry air was used in place of N_2. This would imply that O_2 in the air inhibited the generation of radical species such as $SiMe_3$ radical.

Previously, Hidai's group reported the synthesis of a series of silyldiazenido complexes by the reaction of Mo and W dinitrogen complexes such as **3**, **4**, and **5** with Me_3SiI, Me_3SiCl/NaI, or Me_3SiOTf. It was further revealed that reduction of trans-$[MI(NNSiMe_3)(PMe_2Ph)_4]$ (M = Mo, W) with Na in the presence of Me_3SiCl under Ar affords $N(SiMe_3)_3$ as a principal nitrogenous product.[18,34] We investigated the stoichiometric reaction of **1a** with 1 equiv of Me_3SiOTf (OTf = OSO_2CF_3) at room temperature for 1 h, which gave the corresponding silyldiazenido complex (**8**) in 69% isolated yield (eq 2). When **8** was used as a catalyst in place of **1a**, the TON for $N(SiMe_3)_3$ was 44 (Table 1, run 13). In addition, the stoichiometric reaction of **8** with Na (20 equiv) and Me_3SiCl (20 equiv) under an atmospheric pressure of argon afforded $N(SiMe_3)_3$ in 88% yield based on **8** (eq 3). These results suggest that the diazenido complex **8** can be regarded as a reactive intermediate in the catalytic formation of $N(SiMe_3)_3$.



Theoretical Calculations. In this section, we describe a theoretical study on a mechanism of the conversion of N_2 into $N(SiMe_3)_3$ catalyzed **1a**. We briefly discuss the active silyl species in the reaction solution and then propose a plausible mechanism of the catalytic N_2 conversion. All calculations were carried out by using the Gaussian09 program package.[30] All intermediates proposed in this study were searched on potential energy surfaces by using the hybrid density functional B3LYP method.[31] For optimization, the LANL2DZ and 6-31G(d) basis sets were chosen for the metal atoms (Mo, Fe) and the other atoms, respectively (BS1).[32] Optimized structures were confirmed to have no imaginary frequencies by vibrational analyses. Ancillary depf ligands were included without any simplification. The total charge of **1a** is equal to 0, and thus, the formal charges of Mo and Fe in **1a** are 0 and +2, respectively. To determine the energy profile of the proposed catalytic cycle, we performed single-point calculations at the optimized geometries using the 6-311+G(d) basis set instead of the 6-31G(d) basis set (BS2). Solvation effects (THF) were taken into account by using the polarizable continuum model (PCM).[33] Zero-point energy corrections were applied for enthalpy changes (ΔH_0) and activation energies (E_a) calculated for each reaction step.

1. Active Silyl Species. As mentioned above, $SiMe_3$ radical is a possible active silyl species in the present reaction system. Here we would like to deduce the active silyl species based on theoretical calculations. If the active silyl species is directly generated by the Si−Cl bond cleavage of Me_3SiCl, the heterolysis of Me_3SiCl gives $SiMe_3^+$ and Cl^- (eq 4), while the homolysis gives a pair of $SiMe_3$ and Cl radicals (eq 5):

$$Me_3SiCl \rightarrow Me_3Si^+ + Cl^- \quad (4)$$

$$Me_3SiCl \rightarrow Me_3Si\bullet + Cl\bullet \quad (5)$$

The Si−Cl bond energy in THF is calculated to be 70.2 kcal/mol for the heterolysis and 107.3 kcal/mol for the homolysis at the B3LYP/6-311+G(d) level of theory. The large Si−Cl bond energies for both the homolysis and heterolysis indicate that a neutral Me_3SiCl molecule would give neither $SiMe_3$ cation nor $SiMe_3$ radical at room temperature. We can therefore rule out a reaction mechanism containing "alternative protonation/reduction steps" from consideration, which is commonly accepted for nitrogen fixation catalyzed by Schrock's Mo complex.[19−24]

Here we consider the role of sodium in the reaction mixture. If sodium in the reaction solution reduces Me_3SiCl in advance, the generated Me_3SiCl anion is readily cleaved into $SiMe_3$ radical and Cl anion (eqs 6 and 7):

$$Me_3SiCl \xrightarrow{\text{reduction}} Me_3SiCl^- \quad (6)$$

$$Me_3SiCl^- \rightarrow Me_3Si\bullet + Cl^- \quad (7)$$

From the difference in energy between the optimized structures of Me_3SiCl and Me_3SiCl^-, the adiabatic electron affinity of Me_3SiCl is calculated to be −13.2 kcal/mol. The Si−Cl bond cleavage of Me_3SiCl^- in THF is *exergonic* by 7.3 kcal/mol. These values are in good agreement with the experimental fact that Me_3SiCl molecules slowly generate disilane $Me_3SiSiMe_3$ in the presence of Na in THF. From both the experimental and theoretical results, the following discussion focuses on a radical mechanism in which $SiMe_3$ radical plays a role in the catalysis.

2. Catalytic Mechanism for the Dinitrogen-to-Silylamine Conversion. We present in Figure 1 a plausible mechanism on the conversion of N_2 into $N(SiMe_3)_3$ via successive addition of

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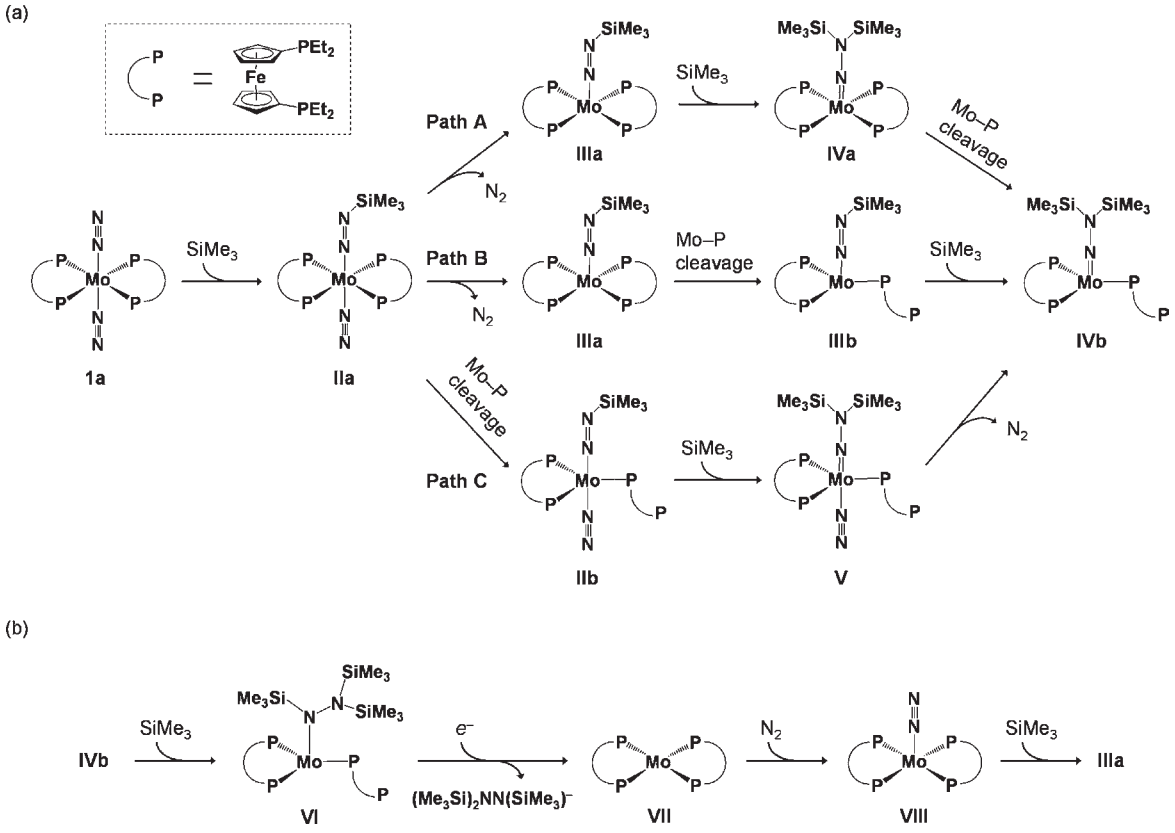

Figure 1. Possible mechanism of the catalytic conversion of N_2 into $N(SiMe_3)_3$ by a molybdenum complex bearing ferrocenyldiphosphines. (a) Three pathways to yield the four-coordinate intermediate **IVb**. (b) The formation of $(Me_3Si)_2NN(SiMe_3)$ anion and the start of the next catalytic cycle. $SiMe_3$ represents trimethylsilyl radical.

$SiMe_3$ radicals, which is partially relevant to Hidai and Mizobe's proposal for *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ **3**.[34] In their catalytic mechanism, a five-coordinate intermediate is first formed by the dissociation of one N_2 ligand in **3**. Figure 2 shows optimized structures of **1a** and intermediates **II**−**VIII** proposed in the present calculation. Figure 3 shows the overall energy profile containing the enthalpy change and activation energy (in parentheses) for each reaction step. Detailed information on the reaction steps, such as optimized structures of reactant complexes, transition states, and product complexes, are described in the Supporting Information. The conversion starts with the addition of $SiMe_3$ to one of the N_2 ligands in **1a** to yield $[Mo(N_2)(NNSiMe_3)(depf)_2]$ **IIa**. There are three possible pathways (paths A−C) leading to the doubly silylated intermediate **IVb** having the $NN(SiMe_3)_2$ group. In paths A and B, **IIa** releases the N_2 ligand to form a five-coordinate intermediate $[Mo(NNSiMe_3)(depf)_2]$ **IIIa**. In path C, on the other hand, one of the four Mo−P bonds in **IIa** is cleaved to form another five-coordinate intermediate **IIb**. In path A, the second $SiMe_3$ radical attacks **IIIa** to yield a five-coordinate intermediate **IVa** having the $NN(SiMe_3)_2$ group, and then one of the Mo−P bonds in **IVa** is cleaved to give a four-coordinate intermediate **IVb**. In path B, one of the Mo−P bonds in **IIIa** is cleaved in advance, and then the generated four-coordinate intermediate **IIIb** is attacked by the second $SiMe_3$ radical for the formation of **IVb**. In path C, the five-coordinate **IIb** accepts the second $SiMe_3$ radical to form $[Mo(N_2)(NN(SiMe_3)_2)(depf)_2]$ **V**. The N_2 ligand in **V** is then dissociated to give **IVb**. The third $SiMe_3$ radical attacks the N atom adjacent to the Mo atom of **IVb**, leading to **VI** having the $Me_3SiNN(SiMe_3)_2$ group. One-electron reduction and the Mo−N bond cleavage of **VI** result in the formation of $[Mo(depf)_2]$ **VII** and $(Me_3Si)_2NN(SiMe_3)$ anion. This anion liberated into the reaction solution would be readily converted into two molecules of $N(SiMe_3)_3$ by Me_3SiCl and $SiMe_3$ radicals. The next cycle of the conversion of N_2 starts with the binding of a new N_2 molecule by **VII**. The addition of $SiMe_3$ radical to $[Mo(N_2)(depf)_2]$ **VIII** gives **IIIa** and the following reactions proceed along path A or B.

3. Addition of first $SiMe_3$ Radical and Formation of Five-Coordinate Intermediates. As shown in Figures 1 and 3, the catalytic cycle starts with the addition of $SiMe_3$ radical to the initial complex **1a**, which is exergonic by 2.6 kcal/mol in THF. The calculated activation barrier (8.3 kcal/mol) is low enough to overcome at room temperature. As mentioned above, there are three possible reaction pathways for the formation of five-coordinate intermediates from the generated intermediate **IIa**: the Mo−N_2 bond dissociation leading to **IIIa** (paths A and B) and the Mo−P bond dissociation leading to **IIb** (path C). As shown in Figure 3, the enthalpy change for the Mo−N_2 bond dissociation of **IIa** (**IIa** → **IIIa**) is calculated to be +2.4 kcal/mol (E_a = 13.7 kcal/mol) in THF, which is much smaller than that for the Mo−N_2 bond dissociation of **1a** (+18.4 kcal/mol; E_a = 20.0 kcal/mol). These values suggest that the silylation of one N_2 ligand prompts the dissociation of the other N_2 ligand. In the Mo−depf system, a five-coordinate intermediate will be formed after the silylation of the initial complex, while the catalytic mechanism proposed for *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ **3** supposed that one N_2 ligand dissociates from **3** before the addition of $SiMe_3$.[20]

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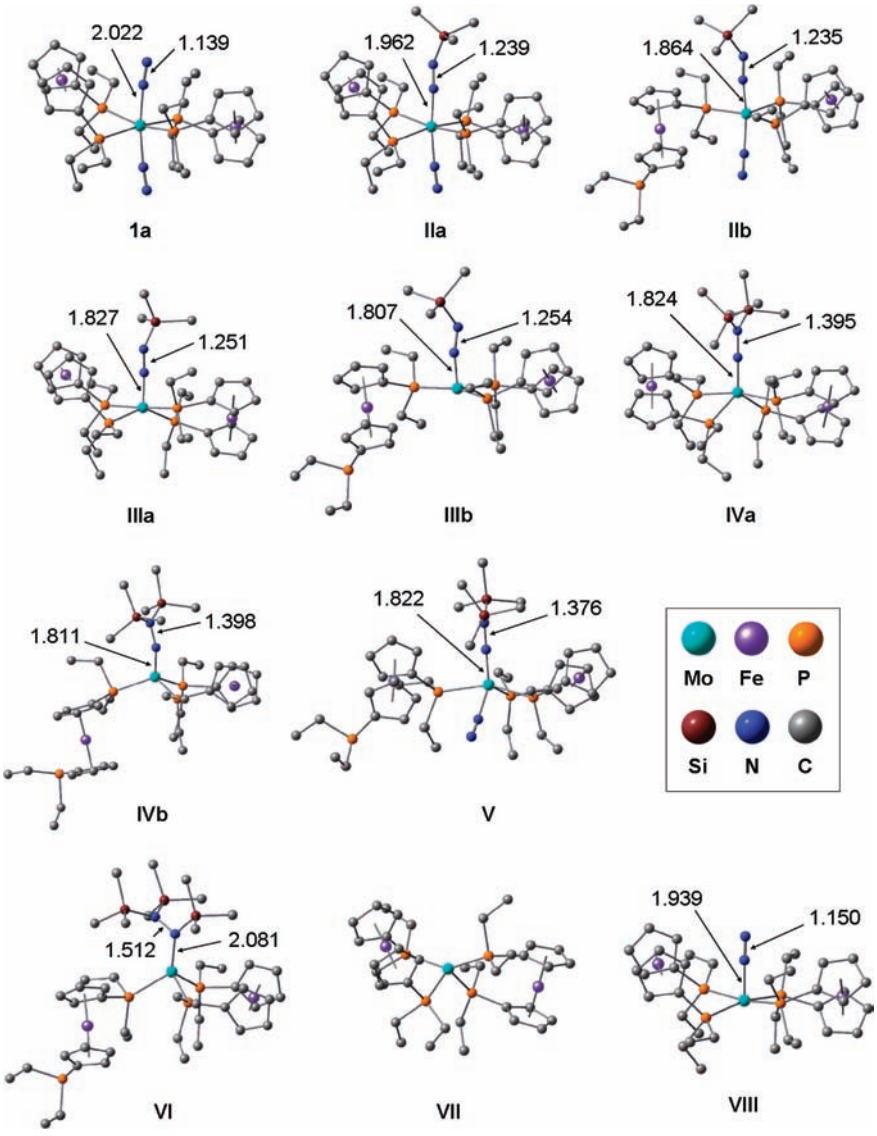

Figure 2. Optimized structures of **1a** and possible intermediates **II**−**VIII**. Hydrogen atoms are omitted for clarity. Interatomic distances are presented in Å.

Figure 4 presents computed energy changes of **1a** and **IIa** plotted as a function of one of the Mo−P bond distances *r*. Optimization at each fixed *r* was carried out at the B3LYP/BS1 level of theory, and the total energy in THF was obtained with a single-point calculation at the B3LYP/BS2 level of theory. For comparison, we show in this figure energy changes calculated for *trans*-$[Mo(N_2)_2(dppe)_2]$ **5** having bidentate phosphine coligands and its silylated complex *trans*-$[Mo(N_2)(NNSiMe_3)(dppe)_2]$ **9**. The Mo−P bond cleavage of **1a** requires E_a of 9.8 kcal/mol, and the corresponding five-coordinate structure (Mo−P = 6.371 Å) is 6.0 kcal/mol less stable than **1a**. The activation energy for the Mo−P cleavage of **5** is calculated to be much higher (18.7 kcal/mol), and the five-coordinate structure (Mo−P = 5.205 Å) is 16.8 kcal/mol less stable than the six-coordinate structure. On the other hand, the silylation of **1a** makes a five-coordinate structure energetically more favorable, probably due to the steric repulsion between the $SiMe_3$ group and the bulky depf ligand; the five-coordinate intermediate **IIb** (Mo−P = 6.876 Å) is 8.5 kcal/mol more stable than **IIa**, and E_a for the Mo−P bond cleavage is only 2.5 kcal/mol. Contrary to **IIa**, the five-coordinate structure of **9** (Mo−P = 5.885 Å) is 1.8 kcal/mol less stable than the six-coordinate one and E_a (8.4 kcal/mol) is much higher than that of **IIa**. If the catalytic formation of $N(SiMe_3)_3$ by **5** proceeds in a similar manner to **1a**, high catalytic ability of **1a** relative to **5** may be explained by facile Mo−P bond cleavage in **IIa** as well as the higher thermodynamic stability of the five-coordinate **IIb** than the six-coordinate **IIa**. This is because one of the Mo−P bonds or the Mo−N_2 bond must be dissociated before accepting the second $SiMe_3$ radical, as mentioned later in subsections 4 and 5.

For the following reaction steps leading to **IVb** having the $NN(SiMe_3)_2$ group, we consider both pathways that start from **IIIa** and **IIb**. The addition of $SiMe_3$ to **IIa** to optimize a "diazene" intermediate having the $Me_3SiN{=}NSiMe_3$ group gave the corresponding intermediate having the $NN(SiMe_3)_2$ group.

4. Formation of Four-Coordinate IVb via IIIa (Paths A and B). An intermediate having the $NN(SiMe_3)_2$ group must dissociate one of the Mo−P bonds to accept the third $SiMe_3$ radical, and therefore, intermediate **IVb** has a four-coordinate structure. As shown in Figure 1, two reaction pathways are possible to lead

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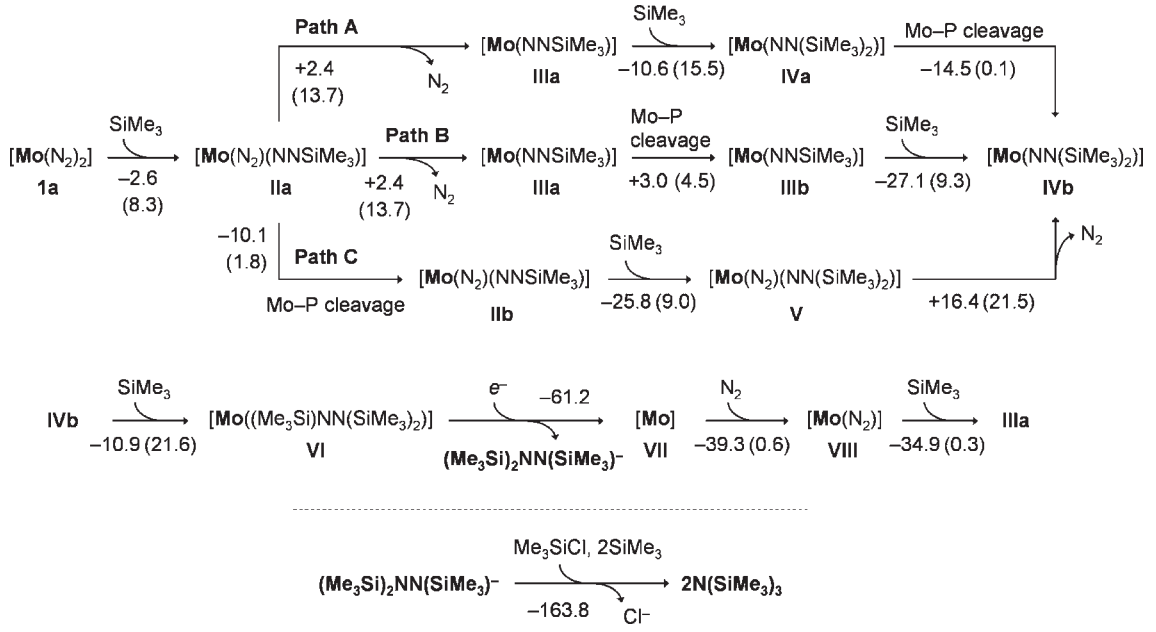

Figure 3. Energy profile of the catalytic conversion of N_2 into $N(SiMe_3)_3$ by **1a**. [Mo] and $SiMe_3$ represent $[Mo(depf)_2]$ and trimethylsilyl radical, respectively. The enthalpy change ΔH_0 and activation energy (E_a, in parentheses) for each reaction step were calculated at the B3LYP/BS2 level of theory, and solvation effects (THF as a solvent) were taken into account. The energies are presented in kcal/mol.

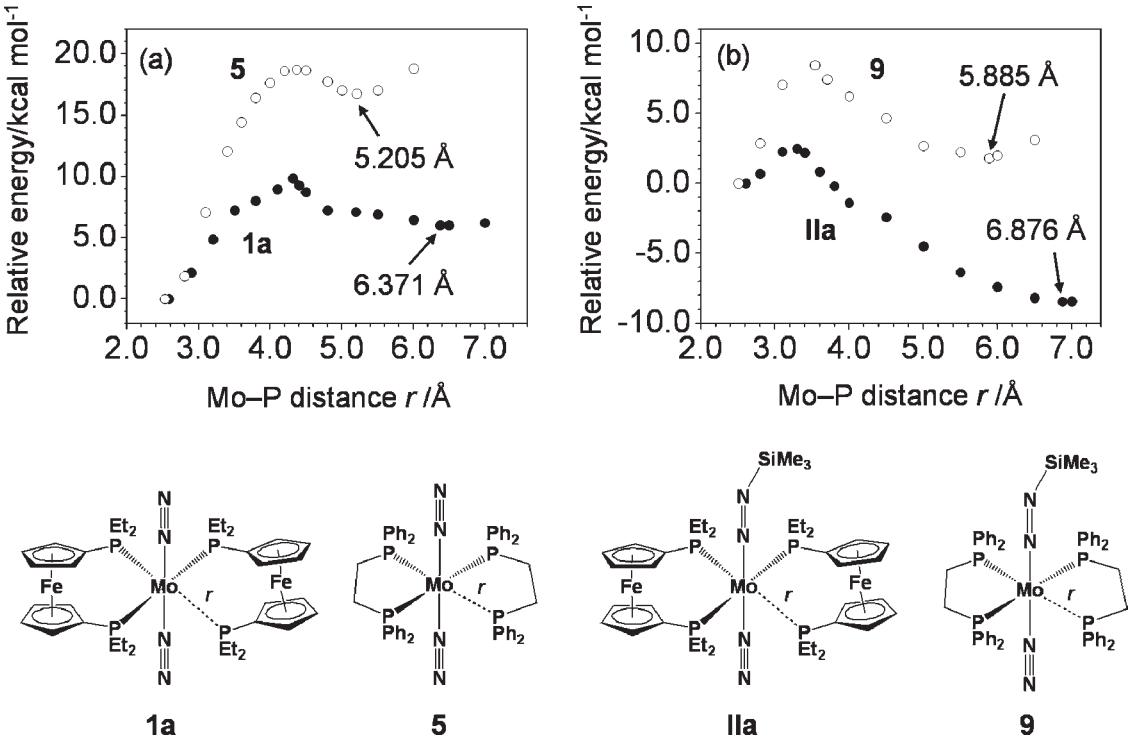

Figure 4. Energy changes for a Mo−P bond cleavage in (a) **1a** and **5** and (b) their silylated complexes **IIa** and **9**. Units are presented in kcal/mol.

to **IVb** from **IIIa**: The addition of $SiMe_3$ to **IIIa** is followed by the Mo−P bond cleavage (path A; **IIIa** → **IVa** → **IVb**). In the other pathway, one of the Mo−P bonds in **IIIa** is dissociated in advance, and then $SiMe_3$ radical attacks to form **IVb** (path B; **IIIa** → **IIIb** → **IVb**). As shown in Figure 3, the addition of $SiMe_3$ to **IIIa** yielding **IVa** is calculated to be an exergonic reaction (ΔH_0 = −10.6 kcal/mol) with a moderate E_a (15.5 kcal/mol). The five-coordinate **IVa** having the bulky $NN(SiMe_3)_2$ group readily dissociates one Mo−P bond to give the four-coordinate **IVb** (ΔH_0 = −14.5 kcal/mol, E_a = 0.1 kcal/mol). In path B, the Mo−P bond cleavage of **IIIa** proceeds in an endergonic way by 3.0 kcal/mol and is hampered by a low activation barrier (4.5 kcal/mol). Instead, the addition of the second $SiMe_3$ radical to **IIIb** yielding **IVb** is a highly exergonic reaction (ΔH_0 = −27.1 kcal/mol) with E_a of 9.3 kcal/mol, which is lower than that for **IIIa** → **IVa**. The calculated ΔH_0 and E_a values

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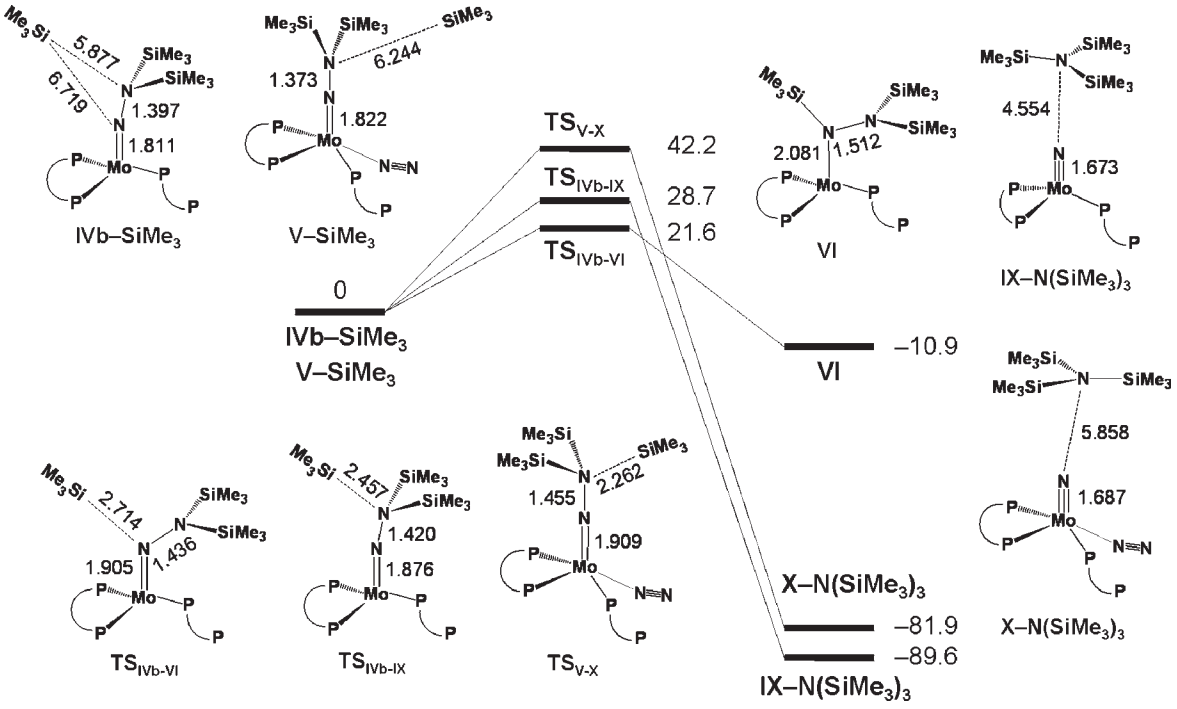

Figure 5. Energy diagrams for the addition of $SiMe_3$ radical to **IVb** and **V**. Interatomic distances and relative energies are presented in Å and kcal/mol, respectively.

suggest that the formation of **IVb** undergoes via both the pathways.

The experimental result that *trans*-[Mo(NNSiMe$_3$)(OTf)(depf)$_2$] **8** served as a catalyst for the formation of N(SiMe$_3$)$_3$ implies that a Mo−Cl species such as *trans*-[Mo(NNSiMe$_3$)(Cl)(depf)$_2$] could be considered as an intermediate, although such a silyldiazenido intermediate was not observed. If this intermediate is reduced by Na, **IIIa** will be formed via the elimination of Cl anion. The enthalpy change for reaction [Mo(NNSiMe$_3$)(Cl)(dppe)$_2$]$^-$ → **IIIa** + Cl$^-$ is calculated to be −16.6 kcal/mol in THF at the B3LYP/BS2//B3LYP/BS1 level of theory. The calculated result also suggests a possibility that *trans*-[Mo(NNSiMe$_3$)(Cl)(depf)$_2$] was temporally formed in the reaction solution.

5. Formation of Four-Coordinate Intermediate IVb via IIb (Path C). Another pathway leading to **IVb** starts from the five-coordinate intermediate **IIb**, in which the Mo center has one Mo−N bond with the N_2 ligand and three Mo−P bonds with two depf ligands (Figure 1). As shown in Figure 3, the addition of the second $SiMe_3$ radical to **IIb** gives intermediate **V** having the NN(SiMe$_3$)$_2$ group, which is exergonic by 25.8 kcal/mol (E_a = 9.0 kcal/mol). All attempts to optimize a six-coordinate structure of **V** having four Mo−P bonds resulted in failure. This is a reason why we considered the formation of the five-coordinate intermediates **IIIa** and **IIb**. The dissociation of N_2 in **V** to give **IVb** proceeds in an endergonic way (ΔH_0 = +16.4 kcal/mol) and has a relatively high activation barrier (21.6 kcal/mol). Although this reaction step seems undesirable from both thermodynamic and kinetic points of view, addition of the third $SiMe_3$ radical to the Mo−Fe system does not occur at room temperature without considering this process, as described later in subsection 6.

6. Addition of Third SiMe$_3$ Radical. As shown in Figure 1, intermediates **IVb** and **V** have two N atoms that can be attacked by $SiMe_3$ radical. If $SiMe_3$ radical attacks the N atom adjacent to the Mo center, a "hydrazido(1−)" intermediate having the Me$_3$SiNN(SiMe$_3$)$_2$ group is formed. On the other hand, the silylation of the doubly silylated N atom will give a "hydrazidium" intermediate having the NN(SiMe$_3$)$_3$ group or cause the N−N bond dissociation to generate a N(SiMe$_3$)$_3$ molecule and a nitrido (≡N) intermediate. Figure 5 displays energy diagrams for the $SiMe_3$ addition to **IVb** and **V**. The silyl addition to the N atom adjacent to the Mo center in **IVb** yields **VI** via **TS$_{IVb-VI}$**. It is noteworthy that **TS$_{IVb-VI}$** and **VI** adopt unique bent Mo−N−N linkages whose angles are 127.0° and 106.2°, respectively. The Mo−N and N−N bond distances in **VI** are calculated to be 2.081 and 1.512 Å, respectively, implying that the Me$_3$SiNN(SiMe$_3$)$_2$ group is still bound to the Mo center; the formation of **VI** is exergonic by 10.9 kcal/mol with E_a of 21.6 kcal/mol.

The silyl addition to the doubly silylated N atom in **IVb** causes a spontaneous cleavage of the N−N bond due to the bulkiness of the generated N(SiMe$_3$)$_3$ moiety and then gives the first molecule of N(SiMe$_3$)$_3$ and the nitrido intermediate **IX**. Although this reaction is highly exergonic (ΔH_0 = −89.6 kcal/mol) relative to the formation of **VI**, the activation barrier of 28.7 kcal/mol seems too high for a reaction occurring at room temperature. Intermediate **V** also undergoes a spontaneous N−N bond dissociation by the addition of $SiMe_3$. The formation of **X** and N(SiMe$_3$)$_3$ is highly exergonic by 81.9 kcal/mol, but the activation barrier of 42.2 kcal/mol is too high to overcome at room temperature, suggesting that a five-coordinate structure is not suitable for the third $SiMe_3$ addition. We did not obtain any intermediate or transition state having the Me$_3$SiNN(SiMe$_3$)$_2$ group for the addition of $SiMe_3$ to **V**.

Intermediate **VI** is not able to accept any more $SiMe_3$ radical, and thus, the Mo−N bond is cleaved to release the Me$_3$SiNN(SiMe$_3$)$_2$ group. Elongation of the Mo−N bond by partial optimizations invoked heterolysis to form Me$_3$SiNN(SiMe$_3$)$_2^-$. In fact, the enthalpy change for the homolysis of the Mo−N

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bond in **VI** (**VI** → **VII** + $Me_3SiNN(SiMe_3)_2$) is +3.9 kcal/mol (endergonic) in THF at the B3LYP/BS2 level of theory, while that for the heterolysis of **VI** (**VI** → **VII**$^+$ + $Me_3SiNN(SiMe_3)_2^-$) is −52.9 kcal/mol (highly exergonic). The cationic **VII** would be readily neutralized by sodium in the reaction solution because the neutral **VII** is 8.3 kcal/mol energetically more favorable than the cation. There is another reaction pathway that **VI** is reduced by sodium in advance and then the anionic **VI** releases $Me_3SiNN(SiMe_3)_2^-$. The anionic **VI** is 45.5 kcal/mol lower in energy than the neutral **VI**, and the Mo−N bond cleavage of the anionic **VI** is exergonic by 15.7 kcal/mol. In total, the one-electron reduction and Mo−N bond cleavage of **VI** to yield **VII** and $Me_3SiNN(SiMe_3)_2^-$ proceed in an exergonic way by 61.2 kcal/mol. $Me_3SiNN(SiMe_3)_2^-$ liberated into the reaction solution will be converted into two molecules of $N(SiMe_3)_3$ by Me_3SiCl and $SiMe_3$ radicals; the enthalpy change for reaction $Me_3SiNN(SiMe_3)_2^- + Me_3SiCl + 2SiMe_3 \rightarrow 2N(SiMe_3)_3 + Cl^-$ is calculated to be −163.8 kcal/mol in THF. The calculated results suggest that **1a** mediates the conversion of N_2 into $N(SiMe_3)_3$ in a different manner from the Yandulov−Schrock mechanism containing a stepwise generation of NH_3 via a nitrido intermediate.[19]

7. Starting the Next Cycle of N_2 Conversion. As shown in Figures 1 and 3, Intermediate **VII** traps a new N_2 molecule at its Mo center to initiate the next cycle of the N_2 conversion. The binding of N_2 proceeds in an exergonic way (ΔH_0 = −39.3 kcal/mol) as virtually a barrierless reaction (E_a = 0.6 kcal/mol). The generated intermediate **VIII** is silylated to form intermediate **IIIa** (ΔH_0 = −34.9 kcal/mol, E_a = 0.3 kcal/mol), and the following reaction steps proceed along path A or B. In conclusion, the rate-determining step in all the reaction steps examined here is the addition of the third Si radical to **IVb** yielding intermediate **VI** (E_a = 21.6 kcal/mol).

CONCLUSIONS

A molybdenum−N_2 complex bearing ancillary ferrocenyldiphosphine ligands, *trans*-$[Mo(N_2)_2(depf)_2]$ **1a**, has catalyzed the conversion of N_2 into $N(SiMe_3)_3$ in the presence of Me_3SiCl and Na at room temperature. The turnover number for the $N(SiMe_3)_3$ generation finally reached 226 for 200 h, which is greatly improved relative to the precedent molybdenum and tungsten complexes having mono- and diphosphine ligands, such as $[M(N_2)_2(PMe_2Ph)_4]$ and $[M(N_2)_2(dppe)_2]$ (M = Mo, W).[18] This is so far the most efficient conversion of N_2 into NH_3 equivalent under ambient conditions. With an assumption that $SiMe_3$ radical works as an active silyl species in the catalytic cycle, we have shown a plausible mechanism of the N_2 conversion by DFT calculations and determined the energy profile of the catalytic cycle from both thermodynamic and kinetic points of view. Almost all of the reaction steps proceed in an exergonic way with reasonably low activation barriers, even the first silylation of N_2. It is notable that the formation of five-coordinate intermediates is essential in an early stage of the conversion. The first silylation of one N_2 ligand in **1a** prompts bond dissociation between Mo and N_2 as well as Mo and P, while these bonds in **1a** are strong enough to adopt a six-coordinate structure. For the silylation of intermediate **IVb** having the $NN(SiMe_3)_2$ group, $SiMe_3$ radical will not attack the N atom having two $SiMe_3$ group to form a pair of a nitrido intermediate and $N(SiMe_3)_3$ but attack the N atom adjacent to the Mo center to give intermediate **VI** having the $Me_3SiNN(SiMe_3)_2$ group. The $Me_3SiNN(SiMe_3)_2$ group is released from the Mo complex as $Me_3SiNN(SiMe_3)_2$ anion and the anion in the reaction solution is readily converted into two molecules of $N(SiMe_3)_2$ by Me_3SiCl and $SiMe_3$ radicals. To afford the $Me_3SiNN(SiMe_3)_2$ anion, the Mo−Fe system should be reduced by sodium before or after the Mo−N bond cleavage. Intermediate **VII** traps a single N_2 molecule for starting the next cycle of the $N(SiMe_3)_3$ generation. The catalytic mechanism proposed in this study is different from the Yandulov−Schrock mechanism, in which ammonia is generated step-by-step on their Mo complex. The catalysis of **1a** would be sterically controlled by the depf ligands through not only its bulkiness but also the flexible Mo−P bond that allows the Mo center to adopt various coordination numbers. Although we expected that the depf ligands contribute to the high catalysis electronically through an electron transfer from the ferrocene moiety to the Mo center, such theoretical suggestions have not been obtained in the framework of the radical mechanism. For all the intermediates, the Fe atoms in the depf ligands have the formal charge of +2 in their electronic ground states, and the spin state of the ferrocene moieties is always closed-shell singlet. Nevertheless, both the experimental and theoretical results provide convincing evidence that $SiMe_3$ radical plays a key role in the present reaction system. $SiMe_3$ cation would not work as an active silyl species because of the presence of a strong reductant (Na) as well as the highly endergonic nature of the heterolysis of Me_3SiCl. We therefore conclude that the radical mechanism presented in this report is highly possible for the catalytic N_2 conversion by **1a**. This conclusion does not necessarily exclude different reaction mechanisms. To reconsider the electronic contribution of the depf ligand to the catalytic ability of **1a**, we are currently investigating a mechanism in which Mo complexes are reduced by Na in place of Me_3SiCl and the anionic Mo species react with the neutral Me_3SiCl .

ASSOCIATED CONTENT

Supporting Information. Details on experiments, computed energetics, and structural changes in the proposed reaction steps, Cartesian coordinates for all optimized intermediates, and the complete author list of ref 30. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Ertl, G. In *Catalytic Ammonia Synthesis*; Jennings, J. R., Ed.; Plenum Press: New York, 1991 and references therein. (b) Appl, M. *Ammonia*; Wiley-VCH: Weinheim, 1999 and references therein.

(2) (a) Allen, A. D.; Senoff, C. V. *Chem. Commun.* **1965**, 621. (b) Bottomley, F.; Nyburg, S. C. *Chem. Commun.* **1966**, 897. (c) Senoff, C. V. *J. Chem. Educ.* **1990**, *67*, 368.

(3) (a) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (b) Hidai, M.; Mizobe, Y. *Can. J. Chem.* **2005**, *83*, 358.

(4) (a) Gambarotta, S. *J. Organomet. Chem.* **1995**, *500*, 117. (b) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5298.

(5) (a) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200*–*202*, 379. (b) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (c) Fryzuk, M. D. *Acc. Chem. Res.* **2009**, *42*, 127. (d) Ballmann, J.; Munhám, R. F.; Fryzuk, N. D. *Chem. Commun.* **2010**, *46*, 1013.

(6) Himmel, H.-J.; Reiher, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6264.

(7) Chirik, P. J. *J. Chem. Soc., Dalton Trans.* **2007**, 16.

(8) (a) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527. (b) Bart, S. C.; Chłopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901. (c) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 7212. (d) Knobloch, D. J.; Toomey, H. E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 4248. (e) Pun, D.; Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 14046. (f) Pun, D.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 6047. (g) Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. *Nat. Chem.* **2010**, *2*, 30.

(9) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. *J. Am. Chem. Soc.* **2005**, *127*, 10184.

(10) (a) Curley, J. J.; Sceats, E. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 14036. (b) Curley, J. J.; Cook, T. R.; Reece, S. Y.; Müller, P.; Cummins, C. C. *J. Am. Chem. Soc.* **2008**, *130*, 9394.

(11) (a) Evans, W. J.; Lee, D. S.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2006**, *128*, 14176. (b) Evans, W. J.; Fang, M.; Zucchi, G.; Furche, F.; Ziller, J. W.; Hoekstra, R. M.; Zink, J. I. *J. Am. Chem. Soc.* **2009**, *131*, 11195.

(12) Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5431.

(13) (a) Kawaguchi, H.; Matsuo, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2792. (b) Akagi, F.; Matsuo, T.; Kawaguchi, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8778.

(14) Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 12690.

(15) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature* **1975**, *253*, 39.

(16) Shilov and co-workers reported the catalytic reduction of molecular dinitrogen into hydrazine. For recent reviews, see:(a) Shilov, A. E. *Coord. Chem. Rev.* **1995**, *144*, 69. (b) Shilov, A. E. *Russ. Chem. Bull.* **2003**, *52*, 2555.

(17) Shiina, K. *J. Am. Chem. Soc.* **1972**, *94*, 9266.

(18) (a) Komori, K.; Oshita, H.; Mizobe, Y.; Hidai, M. *J. Am. Chem. Soc.* **1989**, *111*, 1939. (b) Komori, K.; Sugiura, S.; Mizobe, Y.; Yamada, M.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2953. (c) Oshita, H.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 213. (d) Mori, M. *J. Organomet. Chem.* **2004**, *689*, 4210 and references therein.

(19) (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 79. (b) Ritleng, V.; Yandulov, D. V.; Weare, W. W.; Schrock, R. R.; Hock, A. S.; Davis, W. M. *J. Am. Chem. Soc.* **2004**, *126*, 6150.

(20) Cao, Z.; Zhou, Z.; Wan, H.; Zhang, Q. *Int. J. Quantum Chem.* **2005**, *103*, 344.

(21) Studt, F.; Tuczek, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5639.

(22) (a) Le Guennic, B.; Kirchner, B.; Reiher, M. *Chem.—Eur. J.* **2005**, *11*, 7448. (b) Reiher, M.; Le Guennic, B.; Kirchner, B. *Inorg. Chem.* **2005**, *44*, 9640. (c) Schenk, S.; Le Guennic, B.; Kirchner, B.; Reiher, M. *Inorg. Chem.* **2008**, *47*, 3634. (d) Schenk, S.; Reiher, M. *Inorg. Chem.* **2009**, *48*, 1638.

(23) Hölscher, M.; Leitner, W. *Eur. J. Inorg. Chem.* **2006**, 4407.

(24) Magistrato, A.; Robertazzi, A.; Carloni, P. *J. Chem. Theory Comput.* **2007**, *3*, 1708.

(25) (a) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955. (b) Schrock, R. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5512.

(26) (a) Yuki, M.; Miyake, Y.; Nishibayashi, Y.; Wakiji, I.; Hidai, M. *Organometallics* **2008**, *27*, 3947. (b) Yuki, M.; Midorikawa, T.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 4741. (c) Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 5821.

(27) (a) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 506. (b) Nishibayashi, Y.; Takemoto, S.; Iwai, S.; Hidai, M. *Inorg. Chem.* **2000**, *39*, 5946. (c) Nishibayashi, Y; Saito, M.; Uemura, S.; Takekuma, S.; Takekuma, H.; Yoshida, Z. *Nature* **2004**, *428*, 279.

(28) (a) Tanaka, H.; Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y.; Yoshizawa, K. *J. Am. Chem. Soc.* **2008**, *130*, 9037. (b) Tanaka, H.; Ohsako, F.; Seino, H.; Mizobe, Y.; Yoshizawa, K. *Inorg. Chem.* **2010**, *49*, 2464.

(29) Tanaka, H.; Shiota, Y.; Matsuo, T.; Kawaguchi, H.; Yoshizawa, K. *Inorg. Chem.* **2009**, *48*, 3875.

(30) Frisch, M. J.; et al. *Gaussian 09*, revision A.01; Gaussian, Inc.: Wallingford CT, 2009.

(31) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(32) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (d) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. (e) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. (f) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(33) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.

(34) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115.