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Syntheses and Some Reactions of Trimethylsilylated Dinitrogen Complexes of Tungsten and Molybdenum[1)]

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A series of new trimethylsilyldiazenido complexes [MX(NNSiMe$_3$)(L)$_4$] (M=Mo: X=I; M=W: X=CF_3SO_3; L=PMe_2Ph or 1/2 dpe; dpe=$Ph_2PCH_2CH_2PPh_2$) and trimethylsilylhydrazido(2−) complexes [MX$_2$(NNHSiMe$_3$)-(PMe_2Ph)$_3$] (M=Mo: X=I or Br; M=W: X=CF_3SO_3) and [MX(NNHSiMe$_3$)(dpe)$_2$]X (M=Mo: X=I; M=W: X=CF_3SO_3) were prepared by treatment of dinitrogen complexes *cis*-[M(N$_2$)$_2$(PMe_2Ph)$_4$] or *trans*-[M(N$_2$)$_2$(dpe)$_2$] with Me$_3$SiX in benzene. The trimethylsilyl groups on the terminal nitrogen atoms were easily replaced by hydrogen by the reaction with MeOH or H_2O, affording, for example, diazenido and hydrazido(2−) complexes such as [WI(NNH)(dpe)$_2$] and [WI$_2$(NNH$_2$)(PMe_2Ph)$_3$] from [WI(NNSiMe$_3$)(dpe)$_2$] and *mer*-[WI$_2$(NNHSiMe$_3$)-(PMe_2Ph)$_3$], respectively. When reduced with excess Na in THF under N_2, complexes *trans*-[MI(NNSiMe$_3$)-(PMe_2Ph)$_4$] (M=Mo or W) and *mer*-[WI$_2$(NNHSiMe$_3$)(PMe_2Ph)$_3$] gave (Me$_3$Si)$_2$NH and NH_3 in substantial yields, accompanied by the regeneration of the parent dinitrogen complexes. Additional amount of NH_3 was obtained by the hydrolysis of the evaporated reaction mixture residue.

As the first demonstrated example of the Si–N bond formation from coordinated dinitrogen, we have recently reported the reaction of a series of tungsten dinitrogen complexes of the type [W(N$_2$)$_2$(L)$_4$] (L=tertiary phosphines) with Me$_3$SiI to give trimethylsilyldiazenido (NNSiMe$_3$) and trimethylsilylhydrazido(2−) (NNHSiMe$_3$) complexes, together with the X-ray structures of *trans*-[WI(NNSiMe$_3$)(PMe_2Ph)$_4$] (**1**) and *mer*-[WI$_2$(NNHSiMe$_3$)(PMe_2Ph)$_3$] (**2**).[2)] Here we wish

cis-[W(N$_2$)$_2$(PMe_2Ph)$_4$] (**5**) $\xrightarrow{Me_3SiI}$ *trans*-[WI(NNSiMe$_3$)(PMe_2Ph)$_4$] (**1**)

$\xrightarrow{Me_3SiI/HI}$ *mer*-[WI$_2$(NNHSiMe$_3$)(PMe_2Ph)$_3$] (**2**)

to report the results of the reaction of molybdenum dinitrogen complexes *cis*-[Mo(N$_2$)$_2$(PMe_2Ph)$_4$] (**3**) and *trans*-[Mo(N$_2$)$_2$(dpe)$_2$] (**4**, dpe=$Ph_2PCH_2CH_2PPh_2$) with Me$_3$SiI as well as the trimethylsilylation of tungsten dinitrogen complexes *cis*-[W(N$_2$)$_2$(PMe_2Ph)$_4$] (**5**) and *trans*-[W(N$_2$)$_2$(dpe)$_2$] (**6**) by using $CF_3SO_3SiMe_3$. Some properties and reactivities of trimethylsilylated dinitrogen complexes are also described.

Results and Discussion

Preparation of New Trimethylsilylated Dinitrogen Complexes. When treated with 1 equiv of Me$_3$SiI in benzene under rigorously dry conditions, complex **3** gave the trimethylsilyldiazenido complex *trans*-[MoI-(NNSiMe$_3$)(PMe_2Ph)$_4$](**7**) in moderate yield. Complex **3** is more reactive than its tungsten analogue **5**. Thus, the reaction proceeds smoothly even at room temperature, whereas complex **5** does react with Me$_3$SiI around 50 °C. In the case of complex **4**, the reaction is much slower than that of complex **3** under the same conditions and the reaction must be carried out at 50 °C by using 2 equiv of Me$_3$SiI to obtain [MoI-(NNSiMe$_3$)(dpe)$_2$]. As described in the preceding paper,[2)] removal of HI generated in situ by the reaction of Me$_3$SiI and adventitious moisture is necessary to isolate these trimethylsilyldiazenido complexes. On the other hand, if the freeze-pump-thaw cycles to remove HI are omitted, complexes **3** and **4** reacted with Me$_3$SiI (ca. 1.5 equiv for complex **3** and ca. 2 equiv for complex **4**) to give trimethylsilylhydrazido(2−) complexes *mer*-[MoI$_2$(NNHSiMe$_3$)(PMe_2Ph)$_3$](**8**) and [MoI-(NNHSiMe$_3$)(dpe)$_2$]I, respectively, although the isolated yields of these complexes were low. These

[Mo(N$_2$)$_2$(L)$_4$] $\xrightarrow{Me_3SiI}$ [MoI(NNSiMe$_3$)(L)$_4$]

3: L = PMe_2Ph $\xrightarrow{Me_3SiI/HI}$ [MoI$_2$(NNHSiMe$_3$)(L)$_3$] (L = PMe_2Ph)

4: L = 1/2dpe or [MoI(NNHSiMe$_3$)(L)$_4$]I (L = 1/2dpe)

trimethylsilylated dinitrogen complexes of molybdenum are less stable than the corresponding tungsten complexes and decompose slowly at room temperature even when stored under an inert atmosphere in a solid state. The lower isolated yields of the molybdenum complexes than those of the tungsten analogues presumably result from the lower stability observed for the molybdenum complexes.

Spectroscopic data of the trimethylsilyldiazenido and trimethylsilylhydrazido(2−) complexes are shown in Table 1, which correspond well to those of tungsten complexes reported previously (Table 2). It is interesting to note that the trimethylsilyldiazenido complexes of molybdenum show ν(NN) bands at higher frequencies and ν(SiN) bands at lower frequencies than the corresponding tungsten analogues. According to the results of the X-ray analyses of complex **1** which demonstrate the linear W–N–N linkage and the unusually short Si–N bond length in the tri-

Table 1. IR and ^{1}H NMR Data of Trimethylsilylated Dinitrogen Complexes of Molybdenum

Complex	IR[a]				^{1}H NMR[b]
	ν(NN)	δ(CH_3Si)	ν(SiN)	ν(NH)	
trans-[MoI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (**7**)	1610	1245	855	—	0.46 (s, 9H, SiC<u>H</u>$_3$) 1.65 (s, 24H, PC<u>H</u>$_3$)
[MoI(NNSiMe$_3$)(dpe)$_2$]	1660	1230	850	—	c)
mer-[MoI$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$] (**8**)	1345	1255	844	3240	0.04 (s, 9H, SiC<u>H</u>$_3$) 1.39 (d, 6H, PC<u>H</u>$_3$) 2.25 (t, 6H, PC<u>H</u>$_3$) 2.29 (t, 6H, PC<u>H</u>$_3$) 3.60 (s, 1H, N<u>H</u>)
mer-[MoI$_2$(^{15}N^{15}NHSiMe$_3$)(PMe$_2$Ph)$_3$]	1308	1255	844	3240	d)
[MoI(NNHSiMe$_3$)(dpe)$_2$]I·C$_6$H$_6$	1340[f]	1246	843	e)	0.34 (s, SiC<u>H</u>$_3$) 2.64 (broad s, PC<u>H</u>$_2$) 2.76 (broad s, PC<u>H</u>$_2$)
mer-[MoBr$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$]	1341	1251	842	3180	d)

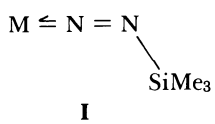
a) cm^{-1}; KBr disks. b) δ; C_6D_6 solution; referred to a trace of C_6H_6 in C_6D_6 at δ 7.25; phenyl protons are omitted. c) Practically insoluble in benzene. d) Not measured. e) Not assignable. f) Very weak.

Table 2. IR and ^{1}H NMR Data of Trimethylsilylated Dinitrogen Complexes of Tungsten

Complex	IR[a]				^{1}H NMR[b]
	ν(NN)	δ(CH_3Si)	ν(SiN)	ν(NH)	
trans-[W(CF$_3$SO$_3$)(NNSiMe$_3$)(PMe$_2$Ph)$_4$][c]	1565	d)	880	—	0.40 (s, 9H, SiC<u>H</u>$_3$) 1.60 (s, 24H, PC<u>H</u>$_3$)
[W(CF$_3$SO$_3$)(NNSiMe$_3$)(dpe)$_2$]	1638 1665	d)	855	—	e)
mer-[W(CF$_3$SO$_3$)$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$]	1375	d)	845	3255	0.13 (s, 9H, SiC<u>H</u>$_3$) 1.19 (d, 6H, PC<u>H</u>$_3$) 1.70 (t, 6H, PC<u>H</u>$_3$) 1.91 (t, 6H, PC<u>H</u>$_3$) 4.47 (s, 1H, N<u>H</u>)
[W(CF$_3$SO$_3$)(NNHSiMe$_3$)(dpe)$_2$][CF$_3$SO$_3$]	d)	d)	850	3230	0.21 (s, 9H, SiC<u>H</u>$_3$) 2.59 (broad s, PC<u>H</u>$_2$) 2.72 (broad s, PC<u>H</u>$_2$) 5.31 (s, N<u>H</u>)
trans-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (**1**)[f]	1580	1246	873	—	0.47 (s, 9H, SiC<u>H</u>$_3$) 1.73 (s, 24H, PC<u>H</u>$_3$)
[WI(NNSiMe$_3$)(dpe)$_2$][f]	1621	1246	868	—	c)
mer-[WI$_2$(NNHSiMe$_3$)(PMe$_2$Ph)$_3$] (**2**)[f]	1360	1254	842	3250	−0.02 (s, 9H, SiC<u>H</u>$_3$) 1.46 (d, 6H, PC<u>H</u>$_3$) 2.13 (s, 1H, N<u>H</u>) 2.29 (2t, 12H, PC<u>H</u>$_3$)
[WI(NNHSiMe$_3$)(dpe)$_2$]I[f]	1355	1248	842	3195	c)

a) cm^{-1}; KBr disks. b) δ; C_6D_6 solution; referred to a trace of C_6H_6 in C_6D_6 at δ 7.25; phenyl protons are omitted. c) ^{31}P NMR: singlet at −16 ppm from H_3PO_4. d) Obscured by the strong absorbances of CF_3SO_3 ligands. e) Practically insoluble in benzene. f) Ref. 2.

methylsilyldiazenido moiety, we previously proposed the presence of the contribution of structure **II** toward structure **I** considering the back donation from the metal.[2] The IR data described above indicate that the structure **II** contributes to a greater extent in the tungsten complexes than in the molybdenum analogues. This trend can be well explained by the stronger electron-donating ability of tungsten compared with molybdenum, which is commonly observed.



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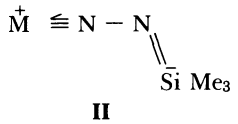
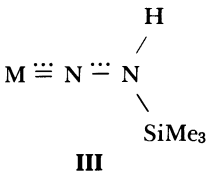


II

In contrast, trimethylsilylhydrazido(2−) complexes of molybdenum show ν(NN)[3] at lower frequencies in the IR spectra than those of the tungsten analogues. In this case also, the greater electron density is presumably donated into the π orbital(s) that spread(s) from the metal to the Si atom via the two nitrogen atoms for the tungsten complexes than the molybdenum analogues. However, this results in an increase of the N–N bond order in contrast to the above trimethylsilyldiazenido complexes. Thus, the structure of the trimethylsilylhydrazido(2−) ligand may best be described as **III**.

When treated with Me$_3$SiBr in place of Me$_3$SiI, complex **3** gave the corresponding trimethylsilylhydrazido-

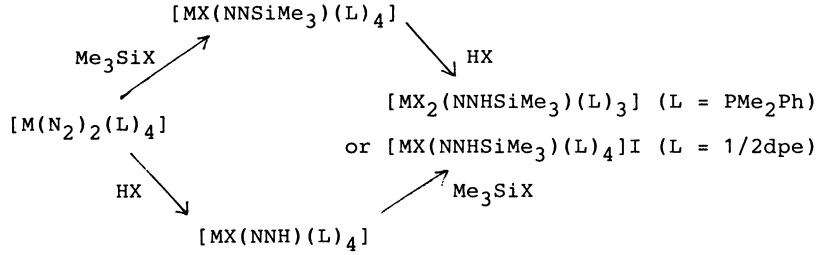


III

(2−) complex *mer*-[$MoBr_2(NNHSiMe_3)(PMe_2Ph)_3$] in low yield. However, no silylated complexes were obtained in the case of complex **5** under the same conditions. On the other hand, complex **5** can be readily converted into trimethylsilylhydrazido(2−) complex *mer*-[$W(CF_3SO_3)_2(NNHSiMe_3)(PMe_2Ph)_3$] by treatment with 3 equiv of $CF_3SO_3SiMe_3$. The reaction proceeded smoothly in benzene at room temperature. However, the trials to isolate the trimethylsilyldiazenido complex *trans*-[$W(CF_3SO_3)(NNSiMe_3)(PMe_2Ph)_4$] by using 1.5 equiv of $CF_3SO_3SiMe_3$ were not successful except for only one run. This is probably because the removal of CF_3SO_3H from $CF_3SO_3SiMe_3$ is very difficult compared to HI. As shown in Table 2, the IR and NMR data are consistent with the above structures. Treatment of complex **6** with 6 equiv of $CF_3SO_3SiMe_3$ at room temperature afforded a mixture of the trimethylsilyldiazenido complex [$W(CF_3SO_3)(NNSiMe_3)(dpe)_2$] and the trimethylsilylhydrazido(2−) complex [$W(CF_3SO_3)(NNHSiMe_3)(dpe)_2$][$CF_3SO_3$]. Appearance of two ν(NN) bands in the IR spectrum of the former complex probably results from the existence of two isomeric forms, for example cis and trans, in this complex. However, this compound is practically insoluble in common NMR solvents and further characterization of this complex was abandoned.

As described above, trimethylsilylhydrazido(2−) complexes can be isolated as the major products in the presence of HX (X=Br, I, CF_3SO_3) that is formed by the reaction of Me_3SiI or $CF_3SO_3SiMe_3$ with adventitious water. This is supported by the fact that when Me_3SiI (3 mol/W atom) in benzene was treated with MeOH (0.8 mol/W atom) first to generate HI in situ and then complex **5** was added to this mixture, the yield of complex **2** increased to 70%. Although this shows that the presence of HX is essential to form trimethylsilylhydrazido(2−) complexes, two reaction pathways are possible as shown below. The pathway which proceeds via [$MX(NNSiMe_3)(L)_4$] is supported by the fact that treatment of complex **1** with 1 equiv of HCl gas gave the trimethylsilylhydrazido(2−) complex [$WClI(NNHSiMe_3)(PMe_2Ph)_3$] which showed ν(NN) and ν(SiN) bands at 1334 and 845 cm^{-1} in its IR spectrum, respectively. On the other hand, the fact that an isolated diazenido complex [$WI(NNH)(dpe)_2$] reacted with Me_3SiI to give [$WI(NNHSiMe_3)(dpe)_2$]I in about 70% yield is indicative of the presence of the other pathway that includes the formation of diazenido complexes (MNNH) and the successive reaction with Me_3SiX. Thus both pathways are possible at present and the reaction course may depend upon the nature of the metals, the phosphines and the trimethylsilylating reagents. At least for the formation of complex **8**, the upper reaction pathway seems more plausible, since complex **7** was isolated as the major product from the reaction of complex **3** with Me_3SiI (2 mol/Mo atom) in the presence of 0.8 equiv of MeOH, whereas the formation of complex **8** was enhanced by the addition of 1.7 equiv of MeOH.

Reaction of Trimethylsilylated Dinitrogen Complexes with Water and Alcohols. As is well-known, trimethylsilyl group has a strong affinity with a fluoride anion and an oxygen atom. Thus, the reaction of complexes **1** and **2** with [*n*-Bu_4N]F were tried, but the purification of the products for full characterization was not successful. In contrast, treatment of complex **2** with about 4 equiv of water in benzene afforded the hydrazido(2−) complex *mer*-[$WI_2(NNH_2)(PMe_2Ph)_3$] (**9**) in 89% yield, as was expected. The similar reaction with a slightly excess of MeOH also resulted in the formation of complex **9** in 66% yield. Furthermore, the trimethylsilyldiazenido complex [$WI(NNSiMe_3)(dpe)_2$] reacted similarly with an almost stoichiometric amount of MeOH to give the diazenido complex [$WI(NNH)(dpe)_2$]. This is the only demonstrated method to derive diazenido complexes from dinitrogen complexes except for the reaction of hydrazido(2−) complexes with weak bases.[4] Diazenido complexes are regarded as an initial intermediate stage to reach ammonia and hydrazine from dinitrogen complexes. Although a series of diazenido complexes of type [$MX(NNH)(dpe)_2$] (M=W: X=F, Cl, Br; M=Mo: X=F, Br) are prepared by the reaction of the corresponding hydrazido(2−) complexes with weak bases, diazenido complexes with PMe_2Ph ligands



are not yet known. Therefore the reaction of complex **1** with water or MeOH was performed. However, the isolated product was only complex **9** (35% yield) for the former and *trans*-[WI(NNH_2)(PMe_2Ph)$_4$]I (15% yield) for the latter, respectively, and the formation of the diazenido complex [WI(NNH)(PMe_2Ph)$_4$] was not observed. It may be presumed that the diazenido complex initially formed was so unstable that it was converted into the hydrazido(2−) complex(es) by the disproportionation reaction. Formation of the dinitrogen complex **5** from the reaction of complex **1** with MeOH may support this reaction pathway, although the yield of complex **5** was quite low.

Redox Properties of Trimethylsilyldiazenido and Trimethylsilylhydrazido(2−) Complexes. Cyclic voltammograms of complexes **1** and **2** were recorded in THF–0.1 M [*n*-Bu_4N][BF_4] under Ar by using glassy carbon, Pt wire and Ag wire immersed in the electrolyte as the working, counter, and reference electrodes, respectively. Under the present conditions, one-electron transfer between (η^5-C_5H_5)$_2$Fe and (η^5-C_5H_5)$_2$Fe$^+$ occurs at the potential of +0.56 V. The solution of the trimethylsilyldiazenido complex **1** shows the irreversible oxidation wave at +1.16 V, which gradually weakened and shifted to the negative direction by the repetitive scans. During these scans appeared the new anodic and cathodic waves at +0.53 and +0.16 V, which may correspond to the redox processes assignable to the species generated by the irreversible oxidation of complex **1**. By the scan to the negative direction from 0 V, no distinctive reduction peaks were observed, although the reduction current itself increased significantly at the potentials below −1.8 V. On the other hand, the trimethylsilylhydrazido(2−) complex **2** shows the irreversible reduction and oxidation waves at −2.1 and +0.82 V, respectively.

Reduction of Trimethylsilylated Dinitrogen Complexes with Sodium Metal and Sodium Hydride. Several attempts have been made to reduce hydrazido(2−) and dialkylhydrazido(2−) complexes to obtain nitrogenous compounds, regenerating the parent dinitrogen complexes at the same time.[5,6] Now we have found that treatment of complex **1** with excess Na sand (0.5—1 mm diameter) in THF at 30 °C under Ar gave $(Me_3Si)_2NH$ and NH_3 in substantial yields, accompanied by the formation of free and coordinated dinitrogen. After hydrolysis of the evaporated reaction mixture residue, additional amount of NH_3 was detected in moderate yield. The total nitrogen balance of the products based on complex **1** as a unit of dinitrogen was 0.95. When this reaction was carried out under N_2, the parent dinitrogen complex **5** was regenerated in 55% yield. The reactions with Na metal proceeded analogously for the molybdenum trimethylsilyldiazenido complex (**7**), the results of which are summarized in Table 3.

$$\textit{trans}\text{-}[MI(NNSiMe_3)(P)_4] \xrightarrow[THF]{Na} N_2 + [M(N_2)_2(P)_4] + (Me_3Si)_2NH + NH_3 + NaNH_2 + (Me_3Si)NHNa + (Me_3Si)_2NNa + \cdots\cdots \quad (M = Mo, W;\ P = PMe_2Ph) \qquad (1)$$

About a half of the nitrogen atoms in the trimethylsilyldiazenido complexes are converted into the N_1 products in this reaction system, with the remainder forming N_2 gas (Eq. 1). Among these products, $(Me_3Si)_2NH$ might be formed by the disproportionation reaction between two unstable Me_3SiNH_2 molecules, the protons of which may be derived from THF and/or a trace amount of H_2O still remaining despite the employment of rigorously dry conditions. Major N_1 products which were detected as NH_3 after hydrolysis are presumably present as the sodium salts such as $NaNH_2$, $Me_3SiNHNa$, or $(Me_3Si)_2NNa$, since the addition of Et_3SiCl to the reaction mixture of complex **1** with Na for 22 h resulted in the formation of Et_3SiNH_2, $(Me_3Si)NH(SiEt_3)$, $(Et_3Si)_2NH$, and $(Me_3$-

Table 3. Reduction of Trimethylsilylated Dinitrogen Complexes[a]

Complex	Atm.	Yield (per metal atom)				
		$(Me_3Si)_2NH$[b]	NH_3		N_2	
			Free	After hydrol.[c]	Free	Coordinated[d]
trans-[WI($NNSiMe_3$)(PMe_2Ph)$_4$] (**1**)	Ar	0.07	0.18	0.67	0.23	0.24
trans-[WI($NNSiMe_3$)(PMe_2Ph)$_4$] (**1**)	N_2	0.03	Trace	0.55	—	e)
trans-[MoI($NNSiMe_3$)(PMe_2Ph)$_4$] (**7**)	Ar	0.09	0.16	0.64	0.50	Trace
trans-[MoI($NNSiMe_3$)(PMe_2Ph)$_4$] (**7**)	N_2	0.11	0.11	0.88	—	e)
trans-[WI($NNSiMe_3$)(PMe_2Ph)$_4$] (**1**)[f]	Ar	0.06	0.65	0.01	0.52	0
trans-[MoI($NNSiMe_3$)(PMe_2Ph)$_4$] (**7**)[f]	Ar	0.05	0.13	0.11	0.50	0.05
mer-[WI_2($NNHSiMe_3$)(PMe_2Ph)$_3$] (**2**)	Ar	0.06	0.02	0.83	0.11	0.14
mer-[WI_2($NNHSiMe_3$)(PMe_2Ph)$_3$] (**2**)	N_2	Trace	0.04	1.00	—	g)

a) Reaction conditions: complex, 0.14—0.17 mmol; THF, 5 ml; Na sand (0.5—1 mm diameter), 20 equiv of M atom; 30 °C, 22 h, in the dark. b) Determined by GLC. c) Not including free NH_3. In each run N_2H_4 was detected in low yields after distillation (ca. 0.06 mol per metal atom). d) Determined by GLC after thermal decomposition and/or by the IR spectrum of the evaporated residue. e) The parent dinitrogen complexes *cis*-[W(N_2)$_2$(PMe_2Ph)$_4$] (**5**) and *cis*-[Mo(N_2)$_2$(PMe_2Ph)$_4$] (**3**) were recovered in 55 and 45% yields, respectively, determined by the IR method. f) NaH was used in place of Na sand. g) *cis*-[W(N_2)$_2$(PMe_2Ph)$_4$] (**5**) were recovered in 36% yield.

$Si)_2N(SiEt_3)$ in the yields of 9%, 21%, 19%, and 6% per W atom, respectively. On the other hand, when complexes **1** and **7** were reduced with Na under Ar in the presence of excess Me_3SiCl, $(Me_3Si)_3N$ was formed as the principal product in the yields of 0.42 mol and 0.75 mol per metal atom, respectively. Based on these observations the catalytic conversion of molecular nitrogen into silylamines has been achieved very recently and details of this work have been reported separately.[7]

Reduction of the trimethylsilylhydrazido(2−) complex **2** with Na metal under the similar reaction conditions also produced $(Me_3Si)_2NH$ and NH_3 in substantial yields together with free N_2 and the parent dinitrogen complex **5** as shown in Table 3. Further NH_3 was detected in moderate yield after following hydrolysis. By the similar treatment under a nitrogen atmosphere, the recovery of the dinitrogen complex **5** increased to 36% per W atom.

When NaH was used as a reducing agent under Ar, about a half of the nitrogen atoms in complexes **1** and **7** were converted into gaseous N_2 and total yields of NH_3 resulting from the remaining nitrogen atoms did not exceed those obtained by the reactions using Na metal.

Experimental

Ganeral. All experiments were carried out under dry nitrogen atmosphere. All solvents were rigorously dried by Na wire or Na–benzophenone ketyl and distilled just before use. Complexes **1**,[2] **2**,[2] **4**,[8] **5**,[8,9] **6**,[8,10] and Me_3SiI[11] were prepared according to the literature methods. Trimethylsilyl triflate commercially obtained was used after being degassed. The IR spectra were recorded on a Hitachi 215 or a Shimadzu IR-400 spectrometer and ^1H and ^{31}P NMR spectra were on a JEOL JMN-GX-400 spectrometer. Quantitative analyses using GLC were carried out on a Hitachi K23, a Shimadzu GC-8A or a GC-14A Gas Chromatograph. GC-MS analyses were performed on a Shimadzu GC-MS QP-1000 spectrometer. Electrochemical measurements were carried out at ambient temperature under Ar by using Hokuto Denko instrumentation (HA-501 Potentiostat, and HB-105 Function Generator), a glassy-carbon working electrode, and a platinum wire counter electrode. Potentials were measured vs. a pseudo-reference electrode of a silver wire immersed in the electrolyte (0.1 M $[n\text{-}Bu_4N][BF_4]$–THF). The cyclic voltammogram recorded under these conditions with the scan rate of $0.2\ V\ s^{-1}$ showed the oxidation potential of ferrocene at $E_{1/2}$=+0.52 V.

Preparation of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$(3). The reported method[8] was modified as follows. The mixture of Mg turnings (6 g) and a piece of I_2 was heated at 150 °C with stirring under reduced pressure for 2 h. After cooling to room temperature, THF (100 ml) and PMe_2Ph (2.85 ml, 20.0 mmol) were added. Then $MoCl_5$ (1.36 g, 5.00 mmol) was added slowly with stirring. The color of the reaction solution changed from pale brown to dark brown. After stirring overnight under N_2 (1 atm) the resultant mixture was filtered and the filtrate was dried up. The dark sticky residue was washed with MeOH, extracted with ether (200 ml) and the extract was cooled down to −20 °C. The yellow crystals deposited were filtered off, washed successively with hexane, MeOH, and ether, and then dried in vacuo (1.2 g, 32%).

The ^{15}N complex *cis*-$[Mo(^{15}N_2)_2(PMe_2Ph)_4]$ was prepared from complex **3** according to the published method.[12]

Preparation of *trans*-$[MoI(NNSiMe_3)(PMe_2Ph)_4]$ (7). Into a solution of Me_3SiI (32 μl, 0.225 mmol) in benzene (5 ml) carefully degassed by freeze (at −50 °C)-pump-thaw cycles was added complex **3** (165 mg, 0.234 mmol) and the resultant yellow solution was stirred for 8 h at room temperature in the dark. Trap to trap condensation of hexane (6 ml) on the red product solution gave red crystals, which were filtered off, washed with hexane and then dried in vacuo (57 mg, 28%). Found: C, 47.25; H, 6.51; N, 2.94; I, 13.98%. Calcd for $C_{35}H_{53}N_2IP_4SiMo$: C, 47.95; H, 6.11; N, 3.19; I, 14.41%.

Preparation of $[MoI(NNSiMe_3)(dpe)_2]$. Into a solution of Me_3SiI (80 μl, 0.56 mmol) in benzene (8 ml) carefully prepared as above was added complex **4** (270 mg, 0.284 mmol). After stirring overnight at 50 °C in the dark, the yellow orange suspension was reduced in volume to a half in vacuo. After trap to trap condensation of hexane (6 ml) on it, the yellow solid deposited was filtered off and dried in vacuo (42 mg, 13%). Found: C, 57.87; H, 4.94; N, 1.49%. Calcd for $C_{55}H_{57}N_2IP_4SiMo$: C, 58.94; H, 5.13; N, 1.49%.

Preparation of *mer*-$[MoI_2(NNHSiMe_3)(PMe_2Ph)_3]$ (8). Into a solution of complex **3** (154 mg, 0.219 mmol) in benzene (5 ml) was added Me_3SiI (49 μl, 0.344 mmol) and the mixture was stirred for 12 h at room temperature in the dark. The deep red solution obtained was filtered and hexane (10 ml) was added to the filtrate by trap to trap condensation. The black crystals precipitated were filtered off, washed with hexane and dried in vacuo (8 mg, 4%). Found: C, 37.10; H, 4.86; N, 2.77; I, 28.72%. Calcd for $C_{27}H_{43}N_2I_2P_3SiMo$: C, 37.43; H, 5.01; N, 3.23; I, 29.29%.

Addition of MeOH (20 μl, 0.493 mmol) into a mixture of Me_3SiI (80 μl, 0.562 mmol) and benzene before reaction with complex **3** (200 mg, 0.284 mmol) increased the yield of complex **8** to 15%.

Preparation of $[MoI(NNHSiMe_3)(dpe)_2]I\cdot C_6H_6$. Into a suspension of complex **4** (502 mg, 0.529 mmol) in benzene (10 ml) was added Me_3SiI (150 μl, 1.05 mmol) and the mixture was stirred for 20 h at 40 °C in the dark. The red product solution was separated from unreacted complex **4** by filtration and hexane (15 ml) was added to the filtrate. Dark yellow crystals deposited were filtered off, washed with hexane, and then dried in vacuo (93 mg, 13%). Found: C, 55.41; H, 5.22; N, 2.10; I, 18.18%. Calcd for $C_{61}H_{64}N_2I_2P_4SiMo$: C, 55.21; H, 4.87; N, 2.11; I, 19.12%.

Preparation of *mer*-$[MoBr_2(NNHSiMe_3)(PMe_2Ph)_3]$. Into a mixture of Me_3SiBr (38 μl, 0.29 mmol) and benzene (7 ml), complex **3** (122 mg, 0.173 mmol) was added to give a yellow solution. After 4 h, the red solution obtained was concentrated and hexane (5 ml) was condensed on it by trap to trap method. On cooling at −18 °C, red crystals precipitated together with crystals of the parent complex **3**. Only the red crystals were collected, washed with hexane and dried in vacuo (5 mg, 4%). Found: C, 42.01; H, 5.55; N, 3.54; Br, 20.73%. Calcd for $C_{27}H_{43}N_2Br_2P_3SiMo$: C, 41.98; H, 5.62; N, 3.62; Br, 20.69%.

Treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$(5) with $CF_3SO_3SiMe_3$.

Into a solution of complex **5** (283 mg, 0.358 mmol) in benzene (5 ml) was added $CF_3SO_3SiMe_3$ (0.195 ml, 1.01 mmol). After stirring for 10 h at room temperature, the resultant red solution was reduced in volume to about a quarter. Trap to trap condensation of hexane (7.5 ml) on it gave red needles of the trimethylsilylhydrazido(2−) complex *mer*-[$W(CF_3SO_3)_2(NNHSiMe_3)(PMe_2Ph)_3$], which were filtered off, washed with hexane and dried in vacuo. (196 mg, 37%). Found: C, 34.42; H, 4.53; N, 2.81%. Calcd for $C_{29}H_{43}O_6N_2F_6S_2P_3SiW$: C, 34.87; H, 4.35; N, 2.81%.

Analogous treatment of complex **5** with 1.5 equiv of $CF_3SO_3SiMe_3$ in benzene gave the trimethylsilyldiazenido complex *trans*-[$W(CF_3SO_3)(NNSiMe_3)(PMe_2Ph)_4$] only once in low yield but all other trials to reproduce this run were unsuccessful probably due to the impurity such as CF_3SO_3H present in the commercially obtained $CF_3SO_3SiMe_3$. Found: C, 44.18; H, 5.44; N, 2.25%. Calcd for $C_{36}H_{53}O_3N_2F_3P_4SSiW$: C, 43.82; H, 5.41; N, 2.84%.

Preparation of [$W(CF_3SO_3)(NNSiMe_3)(dpe)_2$] and [$W(CF_3SO_3)(NNHSiMe_3)(dpe)_2$][$CF_3SO_3$]. Into a suspension of complex **6** (246 mg, 0.237 mmol) in benzene (10 ml) was added $CF_3SO_3SiMe_3$ (0.27 ml, 1.5 mmol) and the mixture was stirred overnight. The resultant orange solution was concentrated to about a half volume and trap to trap condensation of hexane to it gave a mixture of a yellow solid and orange crystals. Removal of the slurry containing the yellow solid remained the orange crystals of the trimethylsilyldiazenido complex, which was washed with hexane and dried (231 mg, 79%). Found: C, 54.88; H, 4.68; N, 2.00%. Calcd for $C_{56}H_{57}O_3N_2F_3SP_4SiW$: C, 54.63; H, 4.68; N, 2.27%. The trimethylsilylhydrazido(2−) complex was isolated by filtration of the separated yellow slurry (42 mg, 13%). Found: C, 48.34; H, 3.90; N, 1.17%. Calcd for $C_{57}H_{58}O_6N_2F_6S_2P_4SiW$: C, 49.57; H, 4.24; N, 2.03%.

Reaction of *trans*-[$WI(NNSiMe_3)(PMe_2Ph)_4$] (1) with HCl Gas. Onto a frozen solution of complex **1** (158 mg, 0.164 mmol) in benzene (10 ml) was condensed HCl gas (107 ml/28 mmHg/22.5 °C, 0.163 mmol; 1 mmHg≈133.322 Pa) at −196 °C. The mixture was slowly warmed to room temperature and stirred for 24 h. The red product solution was concentrated to about 2 ml in vacuo and hexane (6 ml) was added to it by trap to trap condensation. The yellow solid of *mer*-[$WClI(NNHSiMe_3)(PMe_2Ph)_3$] was filtered off, washed with hexane and dried in vacuo (92 mg, 64%). IR (KBr disk): ν(NN), 1334; $\delta(Me_3Si)$, 1245; ν(SiN), 845 cm^{-1}.

Reaction of [$WI(NNH)(dpe)_2$] with Me_3SiI. Into a suspension of [$WI(NNH)(dpe)_2$] (207 mg, 0.182 mmol) in benzene (10 ml) was added Me_3SiI (54 μl, 0.379 mmol). The color of the mixture gradually changed from yellow to orange. After stirring for 6 h, the orange solid was filtered off, washed with hexane and dried in vacuo (199 mg). Major component of this solid was [$WI(NNHSiMe_3)(dpe)_2$]I, the yield of which was estimated to be about 70% by the IR spectrum. Further purification of the product was not successful because of its low solubility.

Reaction of *trans*-[$WI(NNSiMe_3)(PMe_2Ph)_4$] (1) with Water. Into a solution of complex **1** (119 mg, 0.123 mmol) in benzene was added H_2O (2.2 μl, 0.122 mmol) and the mixture was stirred for 17 h in the dark at room temperature. The red solution obtained was concentrated to about 1 ml and hexane (6 ml) was added to it. The brown solid deposited was filtered off and precipitated again from benzene/hexane. The yellow solid isolated was characterized as complex **9** by the IR spectrum and the analytical data (38 mg, 35%). Found: C, 33.01; H, 4.01; N, 3.07%. Calcd for $C_{24}H_{35}N_2I_2P_3W$: C, 32.67; H, 4.01; N, 3.18%.

Reaction of *mer*-[$WI_2(NNHSiMe_3)(PMe_2Ph)_3$] (2) with Water. Analogous treatment of complex **2** (112 mg, 0.116 mmol) in benzene (10 ml) with H_2O (7.5 μl, 0.414 mmol) gave the product suspension. The yellow solid separated by filtration was characterized as complex **9** by the IR spectrum (91 mg, 89%).

Reaction of *mer*-[$WI_2(NNHSiMe_3)(PMe_2Ph)_3$] (2) with MeOH. Into a solution of complex **2** (254 mg, 0.266 mmol) in benzene (5 ml) was added MeOH (13 μl, 0.322 mmol). The red solution changed rapidly to the brown suspension. After stirring for 20 h in the dark, complex **9** produced was filtered off, washed with benzene and dried in vacuo (145 mg, 66%).

Reaction of [$WI(NNSiMe_3)(dpe)_2$] with MeOH. Into a suspension of [$WI(NNSiMe_3)(dpe)_2$] (220 mg, 0.182 mmol) in benzene (15 ml) was added MeOH (7.8 μl, 0.193 mmol). After stirring for 35 h, the resultant suspension was filtered and the deep yellow solution obtained was concentrated to about 3 ml. Addition of hexane (7 ml) gave dark red crystals of [$WI(NNH)(dpe)_2$], which were filtered off, washed with hexane and dried in vacuo (42 mg, 20%). Found: C, 55.01; H, 4.30; N, 2.09; I, 11.54%. Calcd for $C_{52}H_{49}N_2IP_4W$: C, 54.94 H, 4.35; N, 2.46; I, 11.16%. IR (KBr disk): ν(NN), 1900 cm^{-1}.

Reaction of *trans*-[$WI(NNSiMe_3)(PMe_2Ph)_4$] (1) with MeOH. Analogous treatment of complex 1 (212 mg, 0.220 mmol) with MeOH (13 μl, 0.322 mmol) gave the brown solid of *trans*-[$WI(NNH_2)(PMe_2Ph)_4$]I (34 mg, 15%). From the filtrate were obtained small amounts of complexes **5** and **9**. However, isolation and characterization of the major product from this reaction mixture were not successful.

Reduction of Trimethylsilylated Dinitrogen Complexes. under Ar with Na: Onto a frozen mixture of THF (5—6 ml) and Na sand (0.5—1 mm diameter, ca. 20 mol excess) in a rigorously dried Schlenk tube with a volume of 35—40 ml, complex **1**, **2**, or **7** (0.12—0.17 mmol) and nonane as an internal standard were added under Ar. The mixture was warmed slowly and then stirred for 22 h in the dark at 30 °C. After determining the amounts of the evolved N_2 in the gaseous phase (Molecular Sieve 13X, 80—100 mesh, 3 mm ϕ×2.0 m stainless column) and $(Me_3Si)_2NH$ in the liquid phase (Silicone KF-96, 5% on Chromosorb W(AW-DMCS), 60—80 mesh, 2.6 mm ϕ×2.0 m glass column) by GLC, volatile materials were condensed into another Schlenk tube immersed in liquid nitrogen from the reaction mixture which was cooled down to −30—−40 °C to avoid the evaporation of $(Me_3Si)_2NH$. The trapped materials including free ammonia were treated with aqueous H_2SO_4 solution (0.5 mol dm^{-3}, 10 ml) and NH_3 was analyzed quantitatively by the indophenol method. As for the evaporated residue, the amount of the coordinated dinitrogen was determined by comparing the intensities of the ν(NN) band at 1910 cm^{-1} and the band at 1430 cm^{-1} assigned to the phenyl group in PMe_2Ph ligand and/or by the GLC analysis of the evolved N_2 gas after thermal decomposition of the residue at 160—170 °C for 1 h. After these procedure, the residue was treated with an aqueous KOH solution (40%, 10 ml) and NH_3 and N_2H_4 distilled into an aqueous H_2SO_4 solution were analyzed by indophenol and *p*-dimethylaminobenzaldehyde reagents, respectively.

Under N_2 with Na: The similar procedure to the reduction under Ar was carried out except for the determination of evolved N_2 gas by GLC.

Under Ar with NaH: The similar procedure was undertaken except that NaH (ca. 20 mol excess) was used in place of Na sand.

Reaction with Et_3SiCl after Reduction. After the similar treatment of complex **1** (141 mg, 0.146 mmol) with Na microdispersion (62 mg, 2.71 mmol) adding decane as an internal standard, the amount of $(Me_3Si)_2NH$ determined by GLC was 0.11 mol per W atom (Silicone OV-17, 5% on Chromosorb W(AW-DMCS), 60—80 mesh, 2.6 mmϕ×2.0 m glass column). Then Et_3SiCl (356 mg, 2.43 mmol) was added to the solution. After stirring for 2 days at room temperature, the amounts of Et_3SiNH_2, $(Me_3Si)NH(SiEt_3)$ (Silicone OV-17, 5% on Chromosorb W(AW-DMCS), 60—80 mesh, 2.6 mmϕ×2.0 m glass column), $(Et_3Si)_2NH$ and $(Me_3Si)_2N(SiEt_3)$ (Shimadzu HiCap-CBP10-M25-025, capillary column) in the solution were determined by GLC.

Reduction of *trans*-[MoI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (7) and *trans*-[WI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (1) with Na in the Presence of Excess Me_3SiCl. Into a degassed mixture of Na microdispersion (8—10 μm diameter, ca. 20 mol excess) and Me_3SiCl (ca. 20 mol excess) in THF (5 ml) at −78 °C, *mer*-[MoI(NNSiMe$_3$)(PMe$_2$Ph)$_4$] (**7**) (123 mg, 0.128 mmol) was added under Ar. After stirring for 22 h at room temperature in the dark, the unreacted Me_3SiCl and about a half of THF were removed by trap-to-trap method. Then the yield of $(Me_3Si)_3N$ in the residue was determined by GLC (Silicone OV-225, 2% on Chromosorb W(AW-DMCS), 80—100 mesh, 2.6 mmϕ×2.0 m glass column) using nonane as an internal standard (0.75 mol per Mo atom). In the presence of excess Me_3SiCl, the quantitative GLC analysis of $(Me_3Si)_3N$ was not successful under the conditions we examined.

By the similar treatment of complex **1**, $(Me_3Si)_3N$ was produced in the yield of 0.42 mol per W atom.

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