will generally be imparted to the products for a given hand of the stereogenic metal center. Thus, (-)-**4** ultimately yields the product which would be expected from allyl addition to the *re*-face of the aldehyde. Consequently, this system should provide a general and predictable route for the formation of homoallylic alcohols with high enantioselectivity.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank M. R. Mazzieri and J. A. John for their assistance.

Catalytic Conversion of Molecular Nitrogen into Silylamines Using Molybdenum and Tungsten Dinitrogen Complexes[1]

Keiko Komori, Hiroyuki Oshita, Yasushi Mizobe, and Masanobu Hidai*

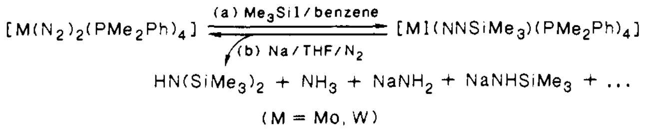
Department of Synthetic Chemistry
University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan

Received October 11, 1988

Although many attempts have been made to develop a system in which molecular nitrogen is catalytically converted into nitrogen hydrides or organonitrogen compounds, the examples reported to date of the effective catalysis by transition-metal complexes under mild conditions are quite rare.[2] Several groups including ours have been studying the reactivities of molybdenum and tungsten dinitrogen complexes of the type $[M(N_2)_2(L)_4]$ (L = tertiary phosphine) and have clarified the details of the attractive reactions such as the protonation and the C-N bond formation at the dinitrogen ligand in these complexes. However, none of these reactions have led to the development of any catalytic nitrogen-fixing systems, since it is difficult to establish the methods to protonate dinitrogen or to form a C-N bond at the dinitrogen ligand accompanied by reducing in situ the high-valent metal species produced by those reactions to the lower oxidation state under the same conditions of the protonation and C-N bond formation reactions.[3] Here we wish to describe initially the formation of the N_1 products concurrent with regeneration of the parent dinitrogen complexes, when trimethylsilylated dinitrogen complexes of Mo and W are reduced with excess Na. This finding has finally led to development of the catalytic system in which molecular nitrogen is converted into silylamines promoted by these dinitrogen complexes.

Previously we reported the preparation of the trimethylsilyldiazenido complexes *trans*-$[WI(NNSiMe_3)(PMe_2Ph)_4]$ (**1**) and $[WI(NNSiMe_3)(dpe)_2]$ by the reactions of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**2**) and *trans*-$[W(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) with Me_3SiI.[4] Analogous treatment of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (**3**) and *trans*-$[Mo(N_2)_2(dpe)_2]$ with Me_3SiI afforded the corresponding molybdenum complexes *trans*-$[MoI(NNSiMe_3)(PMe_2Ph)_4]$ (**4**) and $[MoI(NNSiMe_3)(dpe)_2]$, respectively.[5] These reactions serve as the first example of the Si-N bond formation by reaction at a coordinated dinitrogen moiety.

When complex **1** was treated with excess Na sand (0.5-1 mm diameter) in THF at 30 °C under Ar, $HN(SiMe_3)_2$ and NH_3 were produced in substantial yields accompanied by the formation of free N_2 and a small amount of the parent dinitrogen complex **2**. Further NH_3 was detected in moderate yield after hydrolysis of the evaporated reaction mixture residue. 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 **2** was regenerated in moderate yield. The reactions with Na metal proceeded analogously for complex **4**, the results of which are summarized in Table I.



$$[M(N_2)_2(PMe_2Ph)_4] \underset{(b)\ Na/THF/N_2}{\overset{(a)\ Me_3SiI/benzene}{\rightleftharpoons}} [MI(NNSiMe_3)(PMe_2Ph)_4]$$

$$HN(SiMe_3)_2 + NH_3 + NaNH_2 + NaNHSiMe_3 + \ldots$$

(M = Mo, W)

As a result, about 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. Among these products, $HN(SiMe_3)_2$ might be formed by the disproportionation reaction between two unstable H_2NSiMe_3 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 $NaNH_2$ or $NaNHSiMe_3$, since the addition of Et_3SiCl to the resultant reaction mixture of complex **1** with Na resulted in the formation of Et_3SiNH_2 and $(Et_3Si)(Me_3Si)NH$, which were detected by GC-MS. When complex **1** was reduced with Na under Ar in the presence of excess Me_3SiCl, $N(SiMe_3)_3$ was formed as the principal product in a yield of 0.42 mol per W atom.

These observations led us to investigate the reactions of Me_3SiX and Na in THF in the presence of a catalytic amount of these Mo and W dinitrogen complexes under dinitrogen. To enhance the reaction rate, Na microdispersion (8-10 μ diameter) was used in place of Na sand. The trimethylsilylation of the dinitrogen ligands in complexes **2** and **3** proceeds cleanly for Me_3SiI as described above. However, the reactions using Me_3SiBr and Me_3SiCl were undertaken because Me_3SiI is highly reactive toward THF.[6] When an equimolar amount of Me_3SiBr and Na were reacted at 30 °C in the presence of 1 mol% of complex **3** under dinitrogen, $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ were obtained in 10% (3.2 mol/Mo atom) and 4% (1.8 mol/Mo atom) yields, respectively, accompanied by the formation of $Me_3SiSiMe_3$ and the ring-opening product of THF, $Me_3Si(CH_2)_4OSiMe_3$, as byproducts in substantial yields. When Me_3SiCl was used in place of Me_3SiBr, the yields of the silylamines increased to 24% (7.5 mol/Mo atom) for $N(SiMe_3)_3$ and 1.2% (0.6 mol/Mo atom) for $HN(SiMe_3)_2$. All charged Me_3SiCl was consumed in 4 h under these reaction conditions, and the major byproduct was $Me_3SiSiMe_3$. Therefore the reactions of Me_3SiCl with Na were investigated in further detail.

$$Me_3SiCl + N_2 + Na \xrightarrow[THF]{catalyst} N(SiMe_3)_3 + HN(SiMe_3)_2 + Me_3SiSiMe_3$$

As shown in Table II, complex **3** showed the highest catalytic activity for formation of the silylamines among the complexes examined here, and when the reaction system containing complex **3** (0.05 mmol) was diluted 5 times with THF, the yield of the silylamines was enhanced to 38% (25 mol/Mo atom) accompanied

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(1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 25. Part 24: Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *Chem. Lett.* **1988**, 441.

(2) (a) Hidai, M. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley Interscience: New York, **1985**; Chapter 6. (b) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, **1982**; Vol. 8, p 1073.

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(6) The trimethylsilylation of the dinitrogen ligand in complex **3** also takes place by the reaction with Me_3SiBr, which was confirmed by the isolation of the trimethylsilylhydrazido(2-) complex *mer*-$[MoBr_2(NNHSiMe_3)(PMe_2Ph)_3]$ from the reaction mixture: IR (KBr disk, cm^{-1}) ν(NH), 3180 w; ν(NN), 1341 s; ν(SiN), 843 s; $\delta(SiMe_3)$, 1252 m.

Table I. Reduction of Trimethylsilyldiazenido Complexes with Na Metal[a]

		yield (mol per metal atom)					
		N_2			NH_3		
complex	atm	free	coordinated	$HN(SiMe_3)_2$[b]	free	after hydrol[c]	nitrogen balance[f]
4	N_2		*d*	0.11	0.11	0.88	
	Ar	0.50	tr[e]	0.08	0.16	0.64	0.94
1	N_2		*d*	0.03	tr	0.55	
	Ar	0.23	0.25[e]	0.07	0.18	0.68	0.95

[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. [d] The parent dinitrogen complexes **2** and **3** were recovered in 55% and 45% yields, respectively, determined by the IR method. [e] Determined by GLC after thermal decomposition and/or by the IR spectrum of the evaporated residue. [f] $N_2 + {}^1/_2(HN(SiMe_3)_2 + NH_3)$ in yield (mol per metal atom).

Table II. Effects of Transition-Metal Complexes on the Conversion of Dinitrogen into Silylamines[a]

			yield (%)[b] (turnover number)[c]		
complex	time (h)	conv (%)	$N(SiMe_3)_3$	$HN(SiMe_3)_2$	$(SiMe_3)_2$
none	4	10	0 (0)	0 (0)	2.7
3	4	>95	23.7 (7.5)	1.2 (0.6)	45.1
3[d]	4	84	6.9 (2.4)	0.2 (0.1)	53.4
3[e]	4	>99	21.4 (14.4)	0.9 (0.9)	50.7
3[f]	15	>99	36.6 (24.3)	1.1 (1.1)	39.0
$[Mo(N_2)_2(dpe)_2]$	4	>99	9.7 (3.2)	0.8 (0.4)	53.9
2	4	>99	2.9 (0.9)	1.6 (0.8)	71.8
$[W(N_2)_2(dpe)_2]$	4	>95	3.3 (1.1)	1.4 (0.7)	50.7
$CrCl_3$[d]	4	51	6.3 (2.2)	0.3 (0.2)	25.1
$CrCl_3$[g]	4	37	0.6 (0.2)	0.9 (0.4)	1.4
$MoCl_5$[h]	4	78	0.0 (0.0)	2.0 (1.0)	8.6

[a] Reaction conditions: Me_3SiCl, 10 mmol; Na microdispersion, 10 mmol; THF, 6.5 mL; catalyst, 0.1 mmol; under N_2, 30 °C. The presence of $Me_3SiOSiMe_3$ in 2–9% yield and $Me_3Si(CH_2)_4OSiMe_3$ in 0–3% yield was observed from each reaction mixture. [b] Determined by GLC; (Me_3SiCl converted into the compound)/(Me_3SiCl charged) × 100. [c] Mol per metal atom. [d] Li chips were used instead of Na microdispersion. [e] Catalyst, 0.05 mmol. [f] THF, 32.5 mL; catalyst, 0.05 mmol. [g] $Me_3Si(CH_2)_4OSiMe_3$ was formed in 9.6% yield. [h] $Me_3Si(CH_2)_4OSiMe_3$ was formed in 34.6% yield.

by a decrease in the formation of $Me_3SiSiMe_3$ to 39%.[7] The major byproduct $Me_3SiSiMe_3$ in these reaction mixtures results from the Wurtz-type coupling reaction. Interestingly, this reaction was remarkably enhanced in the presence of the Mo and W complexes. In addition, it should be noted that the yields of silylamines also depends sharply upon the nature of the alkyl groups attached to the Si atom; $EtMe_2SiCl$ can be converted into $N(SiEtMe_2)_3$ catalytically (14%), but Et_3SiCl does not give $N(SiEt_3)_3$ in THF at 30 °C in the presence of 1 mol% complex **3**.

Previously Shiina reported the formation of $N(SiMe_3)_3$ by the reaction of Me_3SiCl and Li in the presence of a series of transition-metal salts under a nitrogen atmosphere, with the highest yield of 5.4 mol per metal atom observed after 30 h using $CrCl_3$ as the catalyst.[8] However, no reaction mechanism was proposed. Compared with this system, the reaction system we have reported here has a considerably greater reaction rate and selectivity toward the silylamine. Interestingly, Na was less effective than Li in the previously reported system, whereas Na was more effective than Li in the present study.

It has already been reported that the complexes *trans*-$[M(N_2)_2(dpe)_2]$ (M = Mo, W) react with alkyl bromides or iodides to give alkyldiazenido complexes $[MX(NNR)(dpe)_2]$[9] and that these alkylation reactions involve the homolysis of the carbon–halogen bond in the intermediate stage $[M(N_2)(dpe)_2(RX)]$ and the subsequent attack of the free radical R$^\bullet$ on the coordinated dinitrogen.[10] This may closely relate to the initiation step of the reaction reported here. Thus the first step of the catalytic cycle for formation of $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ is probably the attack at the terminal nitrogen atom of the coordinated dinitrogen by a trimethylsilyl radical generated from the reaction of Me_3SiCl with Na in the presence of the Mo or W complex. Involvement of the reaction at coordinated dinitrogen in this system was demonstrated by the fact that treatment of complex **3** with Na in the presence of Me_3SiCl under Ar resulted in the formation of $N(SiMe_3)_3$ and $HN(SiMe_3)_2$ in yields of 1.24 and 0.06 mol per Mo atom, respectively. The successive reduction of the silylated dinitrogen complex to the low valent metal species that can again bind a dinitrogen molecule may occur, this being concurrent with the formation of the silylamines.

Although the detail of the reaction mechanism is not yet clear, the reaction system described here is one of the rare examples in which molecular nitrogen is catalytically converted into nitrogen compounds and the involvement of the reaction at coordinated dinitrogen is clarified.

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(7) The reaction rate increased as the temperature was raised in the order of 50 °C > 30 °C > 0 °C, with the selectivity toward the silylamines optimum at 30 °C. Although the yield was much lower than that in THF, the formation of $N(SiMe_3)_3$ was also observed with use of 1,2-dimethoxyethane as the solvent in place of THF, whereas the silylamines were scarcely obtained when the reaction was carried out in benzene.

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Asymmetric Glyoxylate–Ene Reaction Catalyzed by Chiral Titanium Complexes: A Practical Access to α-Hydroxy Esters in High Enantiomeric Purities

Kōichi Mikami, Masahiro Terada, and Takeshi Nakai*

Department of Chemical Technology
Tokyo Institute of Technology
Meguro-ku, Tokyo 152, Japan

Received September 28, 1988

Considerable attention has been focused on the development of asymmetric catalysis for carbon–carbon bond formations in recent years.[1] However, the catalytic asymmetric ene reaction with prochiral glyoxylate, which is potentially useful for asymmetric synthesis of α-hydroxy esters of biological and synthetic importance, has never been developed,[2] while Yamamoto has recently reported a first example of catalytic ene reaction with halogenated aldehydes by using the modified binaphthol-derived aluminum reagent.[3] Herein we wish to report an efficient catalytic enantiocontrol in the glyoxylate–ene reaction as exemplified in eq 1. The key to success is the use as asymmetric catalyst of the chiral titanium complex to be considered type (*R*)-**1**[4] prepared

Table I. Catalytic Ene Reaction of Isobutylene with Methyl Glyoxylate[a]

entry	catalyst, mol %[b]	MS 4A, mg	% yield	% ee (confign)
1[c]	10	500	72	95 (*R*)
2[c]	10	160	72	3 (*R*)
3[c]	10	0	79	7 (*S*)
4[d]	10	0	82	21 (*R*)
5[d]	10	500	74	88 (*R*)

[a] All reactions were run using 1.0 mmol of methyl glyoxylate and 0.1 mmol of Ti complex **2** (X = Cl) and (*R*)-BINOL. [b] Refers to mol % of **2** (X = Cl) used for preparing the chiral catalyst. [c] Carried out via the in situ preparation of the chiral catalyst as described in the text. [d] The chiral complex prepared by benzene azeotropy was used as the catalyst.

0002-7863/89/1511-1940$01.50/0