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
I	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• 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.

[8] Shiina, K. *J. Am. Chem. Soc.* **1972**, *94*, 9266.

[9] Diamantis, A. A.; Chatt, J.; Heath, G. A.; Hooper, N. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1977**, 688.

[10] Chatt, J.; Head, R. A.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1638.

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

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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.

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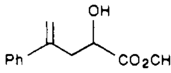
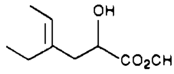
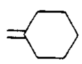
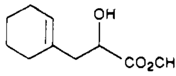
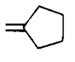
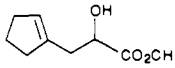
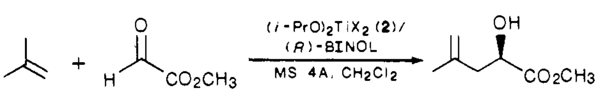
Table II. Catalytic Asymmetric Ene Reactions with Different Olefins[a]

entry	olefin	$(i\text{-PrO})_2TiX_2$ (X)	catalyst, mol %	time, h	product	% yield	% ee[b]
A	$CH_2{=}C(CH_3)_2$	Cl	10	8	**3**	72	95 (*R*)
		Br	10	3		87	83 (*R*)
B	$CH_2{=}C(CH_3)Ph$	Cl	1.0	8		97	97
		Br	1.0	3		98	94
C	$CH_2{=}C(CH_2CH_3)_2$	Cl	10	8		68[c]	75[d]
		Br	5	3		73[c]	98[d]
D		Cl	10	8		82	83
		Br	5	3		89	98
E		Cl	10	8		87	48
		Br	5	3		92	89

[a] All reactions were run by the representative procedure described in the text. [b] Determined by LIS–NMR analysis of the α-methoxy derivative as described in ref 6. The configuration of each major product has not been determined yet but could be assigned to *R* in all cases by the similarity in shift pattern seen in the LIS–NMR spectra using the chiral shift reagent. [c] The combined yield of the *E*- and *Z*-isomer: *E*/*Z* = 89:11 (X = Cl) and 91:9 (X = Br). [d] Refers to the optical purity of the major *E*-product.

in situ from $(i\text{-PrO})_2TiX_2$ (**2**)[1b] and the optically pure binaphthol (BINOL) in the presence of molecular sieves.

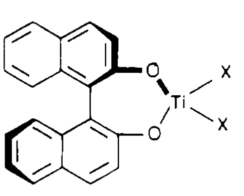


(1)

(*R*)-**3**

(*R*)-**1**, X = Cl (10 mol %), 95% ee

(72% yield)



(*R*)-**1**

The following catalytic procedure is illustrative for the present asymmetric reaction. To a mixture of activated powder molecular sieves 4A (MS 4A)[5] (500 mg) and (*R*)-BINOL[5] (0.10 mmol) in dichloromethane (5 mL) was added a 0.30 M toluene solution (0.33 mL, 0.10 mmol) of $(i\text{-PrO})_2TiCl_2$ at room temperature under argon atmosphere. The mixture was stirred for 1 h and cooled to −70 °C. To the mixture was added successively isobutylene (ca. 2 mmol) and methyl glyoxylate (1.0 mmol). The mixture was then warmed to −30 °C and stirred for 8 h. The resultant mixture was poured into saturated $NaHCO_3$ (10 mL). Usual workup followed by column chromatography furnished the ene product **3** in 72% yield. The enantiomeric purity was determined to be 95% ee by LIS–NMR analysis after conversion to the α-methoxy ester.[6] The configuration of **3** was assigned to *R* through conversion to the known (*R*)-(+)-leucic acid.[5,7] Even a similar use of 1.0 mol % of the catalyst in the presence of MS 4A (500 mg) was found to provide equally satisfactory results (68% yield and 93% ee).

The most striking and puzzling feature of the present asymmetric reaction is the tremendous role of the molecular sieves[8] in determining the optical yield as shown in Table I. The stoichiometry of MS 4A to the catalyst (≥5 g/mmol of the catalyst) is essential for obtaining a high enantioselectivity.[9] Surprisingly enough, the use of the chiral complex (*R*)-**1**[10] independently prepared by benzene azeotropy provides only 21% ee in the absence of MS 4A, as compared with 88% ee in the presence of MS 4A (entries 4 vs 5). Thus these results suggest that the molecular sieves not only facilitates the ligand exchange forming (*R*)-**1**[11] but also plays a vital role in maximizing the stereodifferentiating ability of the chiral catalyst.

The present catalytic method is applicable to various 1,1-disubstituted olefins with high enantioselectivity[12] (Table II). Particularly noteworthy is the significant difference in asymmetric catalysis between the dichloro and dibromo catalysts. The former is lower in reactivity but superior in enantioselectivity for the ene reaction involving a methyl hydrogen, whereas the latter is superior for that involving a methylene hydrogen. Of special interest is entry C where a relatively high (*E*)-selectivity is obtained along with a high enantioselectivity.

Thus, we have developed the asymmetric catalysis for the glyoxylate–ene reaction which provides practical access to α-hydroxy esters in high enantiomeric purities. Further effort is now in progress to probe this interesting but puzzling catalytic process.

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Supplementary Material Available: Experimental details of the catalytic reaction and spectral properties (^1H NMR and IR) of the products (17 pages). Ordering information is given on any current masthead page.

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(1) Review: Bosnich, B. *Asymmetric Catalysis*; Martinus Nijhoff Publishers: Dordrecht, 1986. More recent successes: (a) Aldol: Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Diels–Alder: Narasaka, K.; Inoue, M. Yamada, T. *Chem. Lett.* **1986**, 1967. (c) Hetero-Diels–Alder: Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.

(2) Reported so far is only the substrate-based asymmetric version using a *chiral* glyoxylate and a stoichiometric amount of a Lewis acid: Whitesell, J. K. *Acc. Chem. Res.* **1985**, *18*, 280 and references cited therein.

(3) Maruoka, K.; Hoshino, Y.; Shirasaka, T.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 3967.

(4) A similar type of chiral Ti complex has previously been prepared via reaction of $TiCl_4$ with the dilithium salt of (*R*)-BINOL and used as a catalyst for the aldol and Diels–Alder reactions to provide low optical yields (8–16% ee): Reetz, M. T.; Kyung, S.-H.; Bolm, C.; Zierke, T. *Chem. Ind.* **1986**, 824.

(5) Available from Aldrich Chemical Company, Inc.

(6) Mikami, K.; Kasuga, T.; Fujimoto, K.; Nakai, T. *Tetrahedron Lett.* **1986**, *27*, 4185.

(7) A similar use of (*S*)-BINOL equally available in optically pure form affords (*S*)-**3** in 95% ee (68% yield).

(8) Several catalytic asymmetric reactions have been carried out successfully by the use of MS.[1b,3] Also, see: (a) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922. Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. Sharpless et al. have claimed that a main role of molecular sieves is to protect the catalyst from adventitious water. In our case, however, no significant difference in rate and yield of the ene reaction was observed between the absence and the presence of MS 4A.

(9) We also found that a similar use of 100 mol % of the catalyst vs the glyoxylate (1.0 mmol) provided 5% ee (*S*) with a less amount of MS 4A (0.5 g) but 94% ee (*R*) with an appropriate ratio of MS (5.0 g).

(10) Its ^1H and ^{13}C NMR spectra are essentially identical with those of the Ti complex prepared in situ in the presence of MS 4A. The exact molecular structure of the chiral Ti complex is now under study.

(11) This specific role of MS 4A was confirmed by monitoring the ligand exchange process by ^1H and ^{13}C NMR spectroscopies.

(12) The present catalytic method is not applicable to 1- and 2-butenes; no ene products were obtained under these conditions.