Bull. Chem. Soc. Jpn., 67, 705—709(1994)

# Factor $F_{430}$-Like Catalysis of Ni(tmtaa) (tmtaa=Dianion of 6,8,15,17-Tetramethyl-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine) for Reductive Dehalogenation of Alkyl Halides

Toru ARAI,*,# Kimio KASHITANI, Hiroshi KONDO, and Shigeyoshi SAKAKI
Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto 860

(Received August 30, 1993)

Ni(tmtaa) efficiently catalyzes the reductive dehalogenation of alkyl halide, yielding alkane with either $NaBH_4$ or $NaBH(OMe)_3$ under mild condition. This system is considered to be a model of factor $F_{430}$, the active center of the methyl coenzyme M reductase. Deuterium incorporation into the alkane suggests that the reaction involves not only an electron transfer, but also the nucleophilic substitution of a halide. The ESR spectrum of Ni(tmtaa)/$NaBH_4$ shows the formation of the $Ni^{I}$ species, which is probably a catalytic-active species.

The metal tmtaa (tmtaa=dianion of 6,8,15,17-tetramethyl-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine) complex has attracted much recent attention because of its common characteristics with metalloporphyrin (Scheme 1).[1)] Both tmtaa and porphyrin are dianionic-conjugated ligands with four nitrogen atoms coordinating to the metal. However, the metal tmtaa complex exhibits framework flexibility due to its smaller conjugation, unlike metalloporphyrin. This framework flexibility might allow the central metal to easily change oxidation states.[1a)] Thus, the metal tmtaa complex is expected to serve as a model for metalloenzyme, which metalloporphyrin hardly mimics. Nevertheless, no biomimetic reaction catalyzed by the tmtaa complex has been reported.

Factor $F_{430}$, a nickel complex of a hydrogenated porphyrin, is the active center of the methyl coenzyme M reductase, and participates in the reduction of carbon dioxide to methane.[2)] The key step of catalysis is the reduction of $Ni^{II}$ to $Ni^{I}$, in which the framework flexibility of factor $F_{430}$ is considered to be essential.[2c)] A model reaction of factor $F_{430}$ has scarcely been investigated, except for the electrochemical reduction of alkyl halides by Ni(I) hydroporphyrin.[3)] Because the framework flexibility of Ni(tmtaa) would facilitate the formation of the $Ni^{I}$ species, we attempted to use Ni(tmtaa) in the reductive dehalogenation of alkyl halide as a model of factor $F_{430}$.[4)]

## Experimental

**Materials.** All of the solvents used were dried by appropriate methods and purified by distillation under $N_2$. Alkyl halides were purified by either distillation or recrystallization. Commercially available $NaBH_4$, $NaBD_4$, $NaBH(OMe)_3$, and $NaBH_3CN$ were used without further purification.

**Ni(tmtaa).** Ni(tmtaa) was synthesized from nickel acetate, 1,2-diaminobenzene, and 2,4-pentanedione in refluxing MeOH (48 h) according to the literature,[5)] and was recrystallized from toluene (yield 34%). UV-vis ($CHCl_3$) 587 ($\varepsilon$ 5400), 420 (sh, 12300), 394 (32700), 334 nm (6170). $^1H$NMR ($CDCl_3$) $\delta$=6.70 (4H, dd), 6.57 (4H, dd), 4.86 (2H, s), 2.09 (12H, s). $E_{red}$ (V vs. SCE in DMF) −1.73. Calcd for $C_{22}H_{22}N_4Ni$; C, 65.87; H, 5.53; N, 13.97%. Found: C, 65.99; H, 5.38; N, 13.75%.

**Ni(tmtaa-Me$_4$).** Ni(tmtaa-Me$_4$) (tmtaa-Me$_4$=dianion of 2,3,6,8,11,12,15,17-octamethyl-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine) was synthesized from nickel acetate, 4,5-diamino-*o*-xylene, and 2,4-pentanedione. UV-vis ($CHCl_3$) 588 ($\varepsilon$ 5380), 428 (sh, 16400), 397 (34100) nm. $^1H$NMR ($CDCl_3$) $\delta$=6.47 (4H, s), 4.77 (2H, s), 2.05 (12H, s), 2.04 (12H, s). $E_{red}$ (V vs. SCE) −1.85. Calcd for $C_{26}H_{30}N_4Ni$; C, 68.30; H, 6.61; N, 12.25%. Found: C, 68.01; H, 6.88; N, 12.45%.

**Ni(tmtaa- (COOEt)$_2$).** Ni(tmtaa- (COOEt)$_2$) (tmtaa-(COOEt)$_2$=dianion of diethyl 6,8,15,17-tetramethyl-5,14-dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine-2,11-dicarboxylate) was synthesized from nickel acetate, ethyl 3,4-diaminobenzoate, and 2,4-pentanedione. UV-vis ($CHCl_3$) 594 ($\varepsilon$ 7680), 438 (20700), 404 (44200) nm. $^1H$NMR ($CDCl_3$) $\delta$=7.36 (2H, d), 7.32 (2H, dd), 6.70 (2H, dd), 4.95 (2H, s), 4.29 (4H, q), 2.13 (6H, s), 2.09 (6H, s), 1.33 (6H, t). $E_{red}$ (V vs. SCE) −1.51. Calcd for $C_{28}H_{30}N_4O_4Ni$; C, 61.68; H, 5.55; N, 10.27%. Found: C, 61.90; H, 5.82; N, 10.45%. $^1H$NMR analysis indicated the formation of only one isomer (depicted in Scheme 1) of two possible geometrical isomers.

**Typical Catalytic Reduction.** $NaBH_4$ ($5.0\times10^{-3}$ mol) and Ni(tmtaa) ($5.0\times10^{-5}$ mol) were placed in a flask equipped with a three-way stopcock. After purging the flask with $N_2$, a diglyme (bis(2-methoxyethyl) ether) solution (4.5 $dm^3$) of bromocyclohexane ($2.5\times10^{-3}$ mol) and EtOH (0.5 $dm^3$) were added successively. The reaction was carried out at 30 °C and a small aliquot was withdrawn at appropriate intervals for GLC (a packed column Tween 80) and GC-MS analyses.

**Measurement.** The solution for an ESR measurement was prepared under $N_2$ in a flask equipped with an ESR tube, degassed through freeze-pump-thaw cycles, and transferred to the ESR tube under the degassed condition. The ESR spectra were measured at −196 °C. Cyclic voltammograms were measured with a Pt electrode vs. a saturated calomel electrode (SCE) in DMF containing $1.0\times10^{-2}$ mol $dm^{-3}$ $^nBu_4NClO_4$ at 30 °C.

---

#Present address: Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata, Kitakyushu, 804.

## Results and Discussion

In the presence of $NaBH_4$ and a catalytic amount of Ni(tmtaa), the reductive dehalogenation of various alkyl halides took place in diglyme–10% EtOH (v/v), yielding alkane (Table 1). For instance, turnover numbers (yielded alkane/catalyst) reached 20.0 after 3 h in the reaction of iodocyclohexane (Run 3), where Ni(tmtaa) was $1.0\times10^{-2}$ mol dm$^{-3}$, iodocyclohexane $5.0\times10^{-1}$ mol dm$^{-3}$, and $NaBH_4$ 1.0 mol dm$^{-3}$ (Ni(tmtaa) : iodocyclohexane : $NaBH_4 = 1:50:100$, molar ratio). No alkene was detected and the yield of alkane corresponded to the amount of consumed alkyl halide. Without Ni(tmtaa), no reaction occurred between alkyl halide and $NaBH_4$. Also, no reaction occurred when using Cu(tmtaa)[6] and Ni(tpp) (tpp=5,10,15,20-tetraphenylporphyrinate)[7] instead of Ni(tmtaa). Without a catalyst, the $NaBH_4$-reduction of alkyl halide has been carried out under more vigorous conditions; for instance, 45 °C, 8 h in DMSO for 2-bromopropane.[8] Thus, the efficient catalytic activity of Ni(tmtaa) is worth nothing as model of factor $F_{430}$.

As shown in Table 1, the reductive dehalogenation of chlorocyclohexane took place by Ni(tmtaa)/$NaBH_4$ much more slowly than bromocyclohexane; that of iodocyclohexane occurred more rapidly (Runs 1—3). Also, the reductive dehalogenation of tertiary 1-bromoadamantane was much more slow than that of secondary bromocyclohexane (Runs 2, 5). The half-wave potentials of 1-bromoadamantane and bromocyclohexane (−2.38 and −2.29 V vs. SCE in DMF)[9] are not sufficiently different to account for their reactivities. This fact suggests that not only an electron transfer is involved in the reaction steps. The elementary step is a nucleophilic substitution of halide by hydride, as is considered in the uncatalyzed $NaBH_4$-reduction of alkyl halides.[12] A nucleophilic substitution reaction is consistent with reactivity orders of iodo- > bromo- > chlorocyclohexane and bromocyclohexane > 1-bromoadamantane. In the reduction of iodocyclohexane (Run 3), although the reaction was fast during the initial stage, it was slow during the later stage, since the concentration of the substrate became lower. With a lower concentration of Ni(tmtaa) (Run 4), the turnover numbers increased because the substrate was not dramatically decreased. In reductions of alkyl halides other than iodocyclohexane, no such dependence on the catalyst concentration was observed.

Table 1. Reductive Dehalogenation of Alkyl Halides Catalyzed by Ni(tmtaa)/$NaBH_4$[a]

| Run | Substrate | Turnover numbers[b] | |
|---|---|---|---|
| | | 3 h | 6 h |
| 1 | Chlorocyclohexane[c] | 0 | 0.01 |
| 2 | Bromocyclohexane | 11.3 | 17.9 |
| 3 | Iodocyclohexane | 22.0 | 30.9 |
| 4 | Iodocyclohexane[d] | 37.9 | 66.6 |
| 5 | 1-Bromoadamantane | 0.9 | 1.7 |

a) Ni(tmtaa) = $1.0\times10^{-2}$ mol dm$^{-3}$, Ni(tmtaa) : substrate : $NaBH_4$ = 1 : 50 : 100 in diglyme– 10% EtOH (v/v) at 30 °C, unless otherwise noted. b) Yielded alkane/Ni(tmtaa). c) At 60 °C d) Ni(tmtaa) = $2.0\times10^{-3}$ mol dm$^{-3}$, Ni(tmtaa) : substrate : $NaBH_4$ = 1 : 250 : 500.

Experimental evidence for the nucleophilic substitution of halide was obtained as follows. The reaction of bromocyclohexane with Ni(tmtaa)/$NaBD_4$ in diglyme–10% EtOH yielded a mixture of cyclohexane ($C_6H_{12}$) and [$^2H_1$]cyclohexane ($C_6DH_{11}$) (the conversion of bromocyclohexane was 23% after 3 h). The molar ratio of $C_6H_{12}/C_6DH_{11}$ was 62 : 38 (GS-MS analysis). When an electron transfer occurs from the reduced catalyst, $[Ni^I(tmtaa)]^-$, $Br^-$ eliminates to from $C_6H_{11}\cdot$ (cyclohexyl radical). Hydrogen abstraction by $C_6H_{11}\cdot$ from the solvent or surroundings forms $C_6H_{12}$, although the source of hydrogen is not clear (Eq. 1). On the other hand, the mechanism cannot account for the formation of $C_6DH_{11}$. $BD_4^-$ or $D^-$ coordinating nickel participates in the $S_N2$-type displacement of $Br^-$ (Eq. 2).

$$\text{R-Br} \xrightarrow[\text{Ni}^{\text{II}}\text{(tmtaa)}]{[\text{Ni}^{\text{I}}\text{(tmtaa)}]^-} [\text{R-Br}]^- \longrightarrow \text{R}\cdot + \text{Br}^- \xrightarrow{\text{H}\cdot\text{(solvent)}} \text{RH} \tag{1}$$

$$\text{R-Br} \xrightarrow{\text{D}^-} \text{RD} + \text{Br}^- \tag{2}$$

The reaction of bromocyclohexane with Ni(tmtaa)/$NaBH_4$ in diglyme–10% $C_2D_5OD$ yielded a mixture of $C_6H_{12}$ and $C_6DH_{11}$ (84 : 16). Hydrogen abstraction by $C_6H_{11}\cdot$ and substitution of $Br^-$ by hydride forms $C_6H_{12}$. Deuterium abstraction by $C_6H_{11}\cdot$ from $C_2D_5OD$ forms $C_6DH_{11}$. Thus, the reductive dehalogenation of bromocyclohexane by Ni(tmtaa)/$NaBH_4$ proceeds through two mechanisms: one is an electron transfer from the reduced catalyst; the other is nucleophilic substitution of halide by hydride.

This catalytic reaction was effected by the solvent (Table 2). The reductive dehalogenation of bromocyclohexane hardly took place in diglyme, but smoothly occurred in diglyme–10% MeOH (v/v) (Runs 1, 2). A polar MeOH-containing solvent facilitated the elimination of $Br^-$. In THF–10% MeOH, $NaBH_4$ was not completely dissolved and the reaction was slower than in diglyme–10% MeOH. In DMF–10% MeOH, although $NaBH_4$ was completely dissolved the reaction hardly took place. The strongly coordinating ability of DMF to nickel prevented the reaction. It is necessary to use a solvent that facilitates the elimination of $Br^-$, well dissolves $NaBH_4$, and does not strongly coordinate to nickel. The nature and amount of alcohol were also important. The catalytic activity was according to the

Table 2. Solvent- Effect on Reductive Dehalogenation of Bromocyclohexane Catalyzed by Ni(tmtaa)/$NaBH_4$[a)]

| Run | Solvent (v/v) | Turnover numbers[b)] | |
|---|---|---|---|
| | | 3 h | 6 h |
| 1 | Diglyme | 0 | 0.1 |
| 2 | Diglyme–10% MeOH | 3.2 | 6.2 |
| 3 | THF–10% MeOH[c)] | 1.2 | 2.8 (0.3) |
| 4 | DMF–10% MeOH | 0.04 | 0.2 (0.1) |
| 5 | Diglyme–10% EtOH | 11.3 | 17.9 |
| 6 | Diglyme–10% $^n$PrOH | 1.1 | 4.3 (0.6) |
| 7 | Diglyme–5% EtOH | 18.5 | 24.3 |
| 8 | Diglyme–2% EtOH | 13.6 | 15.9 |

a) Ni(tmtaa)$=1.0\times10^{-2}$ mol dm$^{-3}$, Ni(tmtaa) : bromocyclohexane : $NaBH_4=1:50:100$, at 30 °C. b) Yielded cyclohexane/Ni(tmtaa). Values in parentheses, yielded cyclohexene/Ni(tmtaa). c) $NaBH_4$ is not completely dissolved.

orders' diglyme–10% MeOH < diglyme–10% EtOH > diglyme–10% $^n$PrOH, and diglyme–10% EtOH < diglyme–5%EtOH > diglyme–2% EtOH (Table 2). Strongly protic alcohol (MeOH) and a too large amount of EtOH (10%) disfavored the reaction, probably because protons consumed the active species. In this connection, the reduction of protons to $H_2$ catalyzed by nickel complexes has been reported.[11)] In conclusion, diglyme–5% EtOH was the best solvent for the reductive dehalogenation catalyzed by Ni(tmtaa)/$NaBH_4$.

The catalytic activity also considerably depended on the reductant. When a reductive dehalogenation of bromocyclohexane was carried out by Ni(tmtaa)/NaBH(OMe)$_3$ instead of Ni(tmtaa)/$NaBH_4$, a rapid reaction occurred in diglyme (Table 3, Run 1). Due to the electron-donating character of the methoxyl groups, NaBH(OMe)$_3$ is a stronger donor of hydride.[12)] Therefore, the formation of an active species was easy in the Ni(tmtaa)/NaBH(OMe)$_3$ system and the catalytic reaction took place smoothly, even in diglyme. However, the addition of EtOH to diglyme suppressed the reaction by Ni(tmtaa)/NaBH(OMe)$_3$ (Table 3, Runs 1—6), in contrast with the Ni(tmtaa)/$NaBH_4$ system. EtOH decomposed NaBH(OMe)$_3$ and the catalytic-active species. The Ni(tmtaa)/NaBH(OMe)$_3$ system in diglyme was the most efficient catalytic system examined, and the turnover numbers increased with a lower concentration of Ni(tmtaa); for instance, the turnover number after 3 h was 96.8, where Ni(tmtaa) was $2.0\times10^{-3}$ mol dm$^{-3}$ (Table 3, Run 7). On the contrary, the Ni(tmtaa)/$NaBH_3CN$ system was inefficient (Runs 8, 9), because $NaBH_3CN$ is a very weak hydride donor due to the electron-withdrawing character of the cyano group.[13)]

The catalytic activity depended on the substituent of the tmtaa ligand (Table 4). Ni(tmtaa-(COOEt)$_2$) was less efficient than Ni(tmtaa) for reductive dehalogenation by either $NaBH_4$ or NaBH(OMe)$_3$. The low catalytic activity is due to the less negative reduction potential of Ni(tmtaa-(COOEt)$_2$) (−1.51 V vs. SCE) than Ni(tmtaa) (−1.73 V). [Ni$^{I}$(tmtaa-(COOEt)$_2$)]$^-$ does not have a sufficient ability to reduce bromocyclohexane. On the other hand, although the reduction potential of Ni(tmtaa-Me$_4$) is more negative (−1.85 V) than Ni(tmtaa), Ni(tmtaa-Me$_4$)/$NaBH_4$ was less efficient than Ni(tmtaa)/$NaBH_4$ (Runs 1,5). The active species was formed from Ni(tmtaa-Me$_4$)/$NaBH_4$ to a lesser extent than Ni(tmtaa)/$NaBH_4$, because of the highly negative reduction potential of Ni(tmtaa-Me$_4$). Actually, the turnover numbers increased in the Ni(tmtaa-Me$_4$)/NaBH(OMe)$_3$ system (Run 6), because the strong reductant, NaBH(OMe)$_3$, formed a sufficient amount of [Ni$^{I}$(tmtaa-Me$_4$)]$^-$.

An ESR-measurement provided information concerning the reduced nickel species in the catalytic system. Ni$^{II}$(tmtaa) is ESR-silent, consistent with a planar structure and a low-spin $d^8$ electron configuration.[14)] The ESR spectrum of the Ni(tmtaa)/$NaBH_4$ (1 : 100) mixture in diglyme–5% EtOH showed rhombic signals (Fig. 1a, $g_{\parallel}=2.26$ and $g_{\perp}=2.13$), indicating the formation of the Ni$^{I}$ species. These signals rapidly decreased after the addition of bromocyclohexane, which suggests the catalytic intermediacy of the Ni$^{I}$ species. The reduction of nickel porphyrin is reported to produce a ligand anion radical with an ESR signal at $g=2.0$.[15)] Thus, Ni$^{II}$ can be reduced to Ni$^{I}$ in Ni(tmtaa). The use of flexible Ni(tmtaa) is essential for $F_{430}$-like catalysis. The reduction of Ni(tmtaa) by 2% Na-Hg yielded Na$^+$[Ni$^{I}$(tmtaa)]$^-$ (100 equiv of Na in THF, 0.5

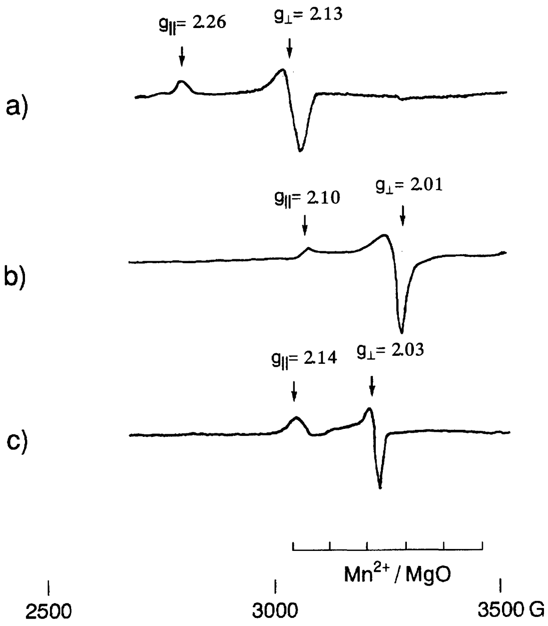

Fig. 1. ESR spectra (at −196°C) of a) Ni(tmtaa)/$NaBH_4$ (1 : 100) in diglyme–5% EtOH, b) Ni(tmtaa)/Na-Hg (1 : 100) in THF, c) Ni(tmtaa)/NaBH(OMe)$_3$ (1 : 100) in diglyme–5% EtOH.

Table 3. Reductive Dehalogenation of Bromocyclohexane with $NaBH(OMe)_3$ and $NaBH_3CN$ Catalyzed by Ni(tmtaa)$^{a)}$

| Run | Reductant | Solvent (v/v) | Ni(tmtaa) | Turnover numbers$^{b)}$ | |
|---|---|---|---|---|---|
| | | | mol dm$^{-3}$ | 3 h | 6 h |
| 1 | $NaBH(OMe)_3$ | Diglyme | $1.0\times10^{-2}$ | 27.5 | 36.4 |
| 2 | $NaBH(OMe)_3$ | Diglyme–2% EtOH | $1.0\times10^{-2}$ | 7.1 | 14.9 |
| 3 | $NaBH(OMe)_3$ | Diglyme–5% EtOH | $1.0\times10^{-2}$ | 6.2 | 12.7 |
| 4 | $NaBH(OMe)_3$ | Diglyme–10% EtOH | $1.0\times10^{-2}$ | 2.3 | 3.1 |
| 5 | $NaBH(OMe)_3$ | Diglyme | $5.0\times10^{-3}$ | 45.5 | 72.9 |
| 6 | $NaBH(OMe)_3$ | Diglyme–2% EtOH | $5.0\times10^{-3}$ | 26.8 | 38.8 |
| 7 | $NaBH(OMe)_3$ | Diglyme | $2.0\times10^{-3}$ | 96.8 | 127 |
| 8 | $NaBH_3CN$ | Diglyme | $1.0\times10^{-2}$ | 0 | 0.2 |
| 9 | $NaBH_3CN$ | Diglyme–5% EtOH | $1.0\times10^{-2}$ | 0 | 0.1 |

a) Bromocyclohexane$=5.0\times10^{-1}$ mol dm$^{-3}$, bromocyclohexane : $NaBH_4=1:2$ at 30 °C. c) Yielded cyclohexane/Ni(tmtaa).

Table 4. Reductive Dehalogenation of Bromocyclohexane Catalyzed by Ni(tmtaa) and Its Derivatives$^{a)}$

| Run | Catalyst | $E_{1/2}$$^{b)}$ | Reductant | Solvent (v/v) | Turnover numbers$^{c)}$ | |
|---|---|---|---|---|---|---|
| | | | | | 3 h | 6 h |
| 1 | Ni(tmtaa) | −1.73 | $NaBH_4$ | Diglyme–5% EtOH | 18.5 | 24.3 |
| 2 | Ni(tmtaa) | | $NaBH(OMe)_3$ | Diglyme | 27.5 | 36.4 |
| 3 | Ni(tmtaa-$(COOEt)_2$) | −1.51 | $NaBH_4$ | Diglyme–5% EtOH | 0.1 | 0.2 |
| 4 | Ni(tmtaa-$(COOEt)_2$) | | $NaBH(OME)_3$ | Diglyme | 1.5 | 4.5 |
| 5 | Ni(tmtaa-$Me_4$) | −1.85 | $NaBH_4$ | Diglyme–5% EtOH | 5.8 | 12.6 |
| 6 | Ni(tmtaa-$Me_4$) | | $NaBH(OMe)_3$ | Diglyme | 23.9 | 27.9 |

a) Catalyst$=1.0\times10^{-2}$ mol dm$^{-3}$, catalyst : bromocyclohexane : $NaBH_4=1:50:100$ at 30 °C. b) V vs. SCE in DMF. c) Yielded cyclohexane/catalyst.

h at 30 °C), showing relatively strong ESR signals at $g_{\parallel}=2.10$ and $g_{\perp}=2.01$ (Fig. 1b).[16] The difference in the ESR spectra between Ni(tmtaa)/$NaBH_4$ (Fig. 1a) and $Na^+[Ni^I(tmtaa)]^-$ (Fig. 1b) suggests that some additional ligand coordinates $Ni^I$ in Ni(tmtaa)/$NaBH_4$. Although the addition of $BH_3$–THF (100 equiv) to $Na^+[Ni^I(tmtaa)]^-$ changed its ESR spectrum to $g_{\parallel}=2.24$ and $g_{\perp}=2.07$, this new spectrum differed from that of Ni(tmtaa)/$NaBH_4$. The additional ligand in Ni(tmtaa)/$NaBH_4$ is not $BH_3$, but may be $H^-$ or $BH_4^-$. The Ni(tmtaa)/$NaBH(OMe)_3$ mixture showed ESR signals at $g_{\parallel}=2.14$ and $g_{\perp}=2.03$ in diglyme–5% EtOH (Fig. 1c), which were somewhat different from Ni(tmtaa)/$NaBH_4$ (Fig. 1a). These ESR spectra of the Ni(tmtaa)/$NaBH_4$ and Ni(tmtaa)/$NaBH(OMe)_3$ systems indicate that some $Ni^I$(tmtaa) complex is the active species of this catalytic reaction, although details concerning the active species are not yet clear.

We thank Mr. Yasuo Hayashida of Kumamoto Industrial Research Institute for the GC-MS measurements. We also thank Dr. Hitoshi Ishida and Mr. Tomoyuki Ohba of Kumamoto University for measurements of the cyclic voltammetry. The present work was supported by Grant-in-Aid for Scientific Research Nos. 03640524 and 04750698 from the Ministry of Education, Science and Culture.

## References

1) a) F. A. Cotton and J. Czuchajowska, *Polyhedron*, **9**, 2553 (1990); b) F. A. Cotton and J. Czuchajowska, *J. Am. Chem. Soc.*, **113**, 3427 (1991); c) S. D. Angelis, E. Solani, E. Gallo, C. Floriani, A. Chiesi-Villa, and C. Rizzoli, *Inorg. Chem.*, **31**, 2520 (1992).

2) a) "The Bioinorganic Chemistry of Nickel," ed by J. R. Lancaster, Jr., VCH, New York (1988); b) A. M. Stolzenberg and M. T. Stershic, *J. Am. Chem. Soc.*, **110**, 6391 (1988); c) M. W. Renner, L. R. Furenlid, K. M. Barkigia, A. Forman, H. K. Shim, D. J. Shimpson, K. M. Smith, and J. Fajor, *J. Am. Chem. Soc.*, **113**, 6891 (1991); d) C. Holliger, A. J. Pierik, E. J. Reijerse, and W. R. Hagen, *J. Am. Chem. Soc.*, **115**, 5651 (1993).

3) A. M. Stolzenberg and M. T. Stershic, *J. Am. Chem. Soc.*, **110**, 5397 (1988); G. K. Lahiri, L. J. Schussel, and A. M. Stolzenberg, *Inorg. Chem.*, **31**, 4991 (1992).

4) Preliminary communication: T. Arai, H. Kondo, and S. Sakaki, *J. Chem. Soc., Dalton Trans.*, **1992**, 2753.

5) V. L. Goedken and M. C. Weiss, *Inorg. Synth.*, **20**, 115 (1980); D. A. Place, G. P. Ferrara, J. J. Harland, and J. C. Dabrowiak, *J. Heterocycl. Chem.*, **17**, 439 (1980); C. L. Bailey, R. D. Bereman, D. P. Rillema, and R. Nowak, *Inorg. Chem.*, **23**, 3956 (1984).

6) F. A. L'Eplattenier and A. Pugin, *Helv. Chim. Acta*, **58**, 917 (1975).

7) E. C. Johnson and D. Dolphin, *Inorg. Synth.*, **20**, 143 (1980).

8) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969).

9) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960); F. L. Lambert, A. H. Albert, and J. P. Hardty, *J. Am. Chem. Soc.*, **86**, 3154 (1964).

10) R. O. Hutchins, F. Dux, III, C. A. Maryanoff, D. Rtostein, B. Goldsmith, W. Burgoyne, F. Cistone, J. Dalessandro, and J. Puglis, *J. Org. Chem.*, **43**, 2259 (1978).

11) L. L. Efros, H. H. Thorp, G. W. Brudvig, and R. H. Crabtree, *Inorg. Chem.*, **31**, 1722 (1992), and references cited therein.

12) H. C. Brown and E. J. Mead, *J. Am. Chem. Soc.*, **75**, 6263 (1953); H. C. Brown, E. J. Mead, and C. J. Shoaf, *J. Am. Chem. Soc.*, **78**, 3616 (1956).

13) R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Am. Chem. Soc.*, **93**, 2897 (1971).

14) C. L. Bailey, R. D. Bereman, D. P. Rillema, and R. Nowak, *Inorg. Chem.*, **23**, 3956 (1984).

15) K. M. Kadish, M. M. Franzen, B. C. Han, C. Araullo-McAdams, and D. Sazuo, *J. Am. Chem. Soc.*, **113**, 512 (1991).

16) S. Ciurli, E. M. Meter, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, **1987**, 281.