

Factor F₄₃₀-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 NaBH₄ or NaBH(OMe)₃ under mild condition. This system is considered to be a model of factor F₄₃₀, 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)/NaBH₄ 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 F₄₃₀, 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 F₄₃₀ is considered to be essential.^{2c)} A model reaction of factor F₄₃₀ 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 F₄₃₀.⁴⁾

Experimental

Materials. All of the solvents used were dried by appropriate methods and purified by distillation under N₂. Alkyl halides were purified by either distillation or recrystallization. Commercially available NaBH₄, NaBD₄, NaBH(OMe)₃, and NaBH₃CN 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 (CHCl₃) 587 (ε 5400), 420 (sh, 12300), 394 (32700), 334 nm (6170). ¹H NMR (CDCl₃) δ=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 C₂₂H₂₂N₄Ni; C, 65.87; H, 5.53; N, 13.97%. Found: C, 65.99; H, 5.38; N, 13.75%.

Ni(tmtaa-Me₄). Ni(tmtaa-Me₄) (tmtaa-Me₄=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 (CHCl₃) 588 (ε 5380), 428 (sh, 16400), 397 (34100) nm. ¹H NMR (CDCl₃) δ=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 C₂₆H₃₀N₄Ni; 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 (CHCl₃) 594 (ε 7680), 438 (20700), 404 (44200) nm. ¹H NMR (CDCl₃) δ=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 C₂₈H₃₀N₄O₄Ni; 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. NaBH₄ (5.0×10⁻³ mol) and Ni(tmtaa) (5.0×10⁻⁵ mol) were placed in a flask equipped with a three-way stopcock. After purging the flask with N₂, a diglyme (bis(2-methoxyethyl) ether) solution (4.5 dm³) of bromocyclohexane (2.5×10⁻³ mol) and EtOH (0.5 dm³) 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 N₂ 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 1.0×10⁻² mol dm⁻³ n-Bu₄NClO₄ at 30 °C.

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

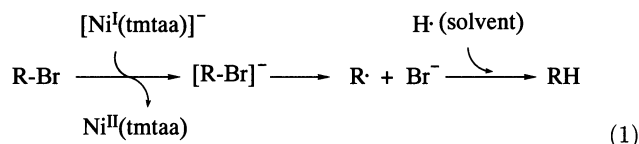
Results and Discussion

In the presence of NaBH_4 and a catalytic amount of $\text{Ni}(\text{tmtaa})$, 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 $\text{Ni}(\text{tmtaa})$ was $1.0 \times 10^{-2} \text{ mol dm}^{-3}$, iodocyclohexane $5.0 \times 10^{-1} \text{ mol dm}^{-3}$, and NaBH_4 1.0 mol dm^{-3} ($\text{Ni}(\text{tmtaa})$:iodocyclohexane: $\text{NaBH}_4 = 1:50:100$, molar ratio). No alkene was detected and the yield of alkane corresponded to the amount of consumed alkyl halide. Without $\text{Ni}(\text{tmtaa})$, no reaction occurred between alkyl halide and NaBH_4 . Also, no reaction occurred when using $\text{Cu}(\text{tmtaa})^{6)}$ and $\text{Ni}(\text{tpp})$ ($\text{tpp} = 5, 10, 15, 20$ -tetraphenylporphyrinate)⁷⁾ instead of $\text{Ni}(\text{tmtaa})$. 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 $\text{Ni}(\text{tmtaa})$ is worth nothing as model of factor F_{430} .

As shown in Table 1, the reductive dehalogenation of chlorocyclohexane took place by $\text{Ni}(\text{tmtaa})/\text{NaBH}_4$ 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 $\text{Ni}(\text{tmtaa})$ (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.

Experimental evidence for the nucleophilic substitution of halide was obtained as follows. The reaction of bromocyclohexane with $\text{Ni}(\text{tmtaa})/\text{NaBD}_4$ in diglyme–10% EtOH yielded a mixture of cyclohexane (C_6H_{12}) and $[^2\text{H}_1]\text{cyclohexane}$ (C_6DH_{11}) (the conversion of bromocyclohexane was 23% after 3 h). The molar ratio of $\text{C}_6\text{H}_{12}/\text{C}_6\text{DH}_{11}$ was 62:38 (GS-MS analysis). When an electron transfer occurs from the reduced catalyst, $[\text{Ni}^{\text{I}}(\text{tmtaa})]^-$, Br^- eliminates to form $\text{C}_6\text{H}_{11}\cdot$ (cyclohexyl radical). Hydrogen abstraction by $\text{C}_6\text{H}_{11}\cdot$ 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 $\text{S}_{\text{N}}2$ -type displacement of Br^- (Eq. 2).



The reaction of bromocyclohexane with $\text{Ni}(\text{tmtaa})/\text{NaBH}_4$ in diglyme–10% $\text{C}_2\text{D}_5\text{OD}$ yielded a mixture of C_6H_{12} and C_6DH_{11} (84:16). Hydrogen abstraction by $\text{C}_6\text{H}_{11}\cdot$ and substitution of Br^- by hydride forms C_6H_{12} . Deuterium abstraction by $\text{C}_6\text{H}_{11}\cdot$ from $\text{C}_2\text{D}_5\text{OD}$ forms C_6DH_{11} . Thus, the reductive dehalogenation of bromocyclohexane by $\text{Ni}(\text{tmtaa})/\text{NaBH}_4$ 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 1. Reductive Dehalogenation of Alkyl Halides Catalyzed by $\text{Ni}(\text{tmtaa})/\text{NaBH}_4$ ^{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) $\text{Ni}(\text{tmtaa}) = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{Ni}(\text{tmtaa})$:substrate: $\text{NaBH}_4 = 1:50:100$ in diglyme–10% EtOH (v/v) at 30°C , unless otherwise noted. b) Yielded alkane/ $\text{Ni}(\text{tmtaa})$. c) At 60°C d) $\text{Ni}(\text{tmtaa}) = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{Ni}(\text{tmtaa})$:substrate: $\text{NaBH}_4 = 1:250:500$.

Table 2. Solvent-Effect on Reductive Dehalogenation of Bromocyclohexane Catalyzed by Ni(tmtaa)/NaBH₄^{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) = 1.0×10^{-2} mol dm⁻³, Ni(tmtaa): bromocyclohexane: NaBH₄ = 1:50:100, at 30 °C. b) Yielded cyclohexane/Ni(tmtaa). Values in parentheses, yielded cyclohexene/Ni(tmtaa). c) NaBH₄ is not completely dissolved.

orders' diglyme-10% MeOH < diglyme-10% EtOH > diglyme-10% ⁿPrOH, 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 H₂ 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)/NaBH₄.

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)/NaBH₄, 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)/NaBH₄ 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 2.0×10^{-3} mol dm⁻³ (Table 3, Run 7). On the contrary, the Ni(tmtaa)/NaBH₃CN system was inefficient (Runs 8, 9), because NaBH₃CN 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 NaBH₄ 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-Me₄) is more negative (−1.85 V) than Ni(tmtaa), Ni(tmtaa-Me₄)/NaBH₄ was less efficient than Ni(tmtaa)/NaBH₄ (Runs 1,5). The active species was formed from Ni(tmtaa-Me₄)/NaBH₄ to a lesser extent than Ni(tmtaa)/NaBH₄, because of the highly negative reduction potential of Ni(tmtaa-Me₄). Actually, the turnover numbers increased in the Ni(tmtaa-Me₄)/NaBH(OMe)₃ system (Run 6), because the strong reductant, NaBH(OMe)₃, formed a sufficient amount of [Ni^I(tmtaa-Me₄)][−].

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)/NaBH₄ (1:100) mixture in diglyme-5% EtOH showed rhombic signals (Fig. 1a, *g*_{||} = 2.26 and *g*_⊥ = 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 F₄₃₀-like catalysis. The reduction of Ni(tmtaa) by 2% Na-Hg yielded Na⁺[Ni^I(tmtaa)][−] (100 equiv of Na in THF, 0.5

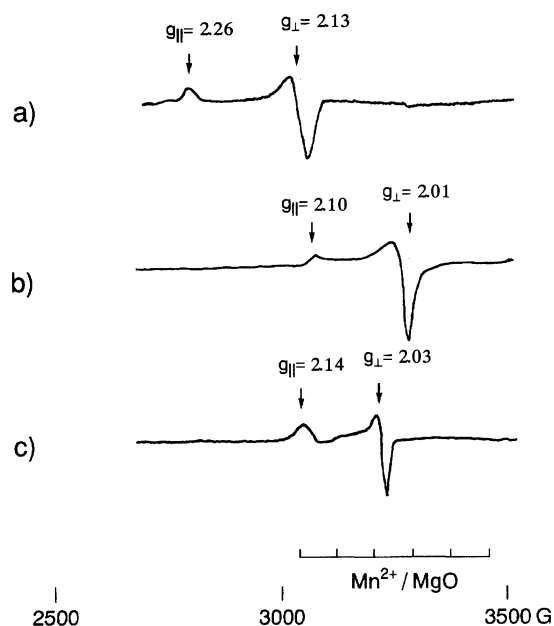


Fig. 1. ESR spectra (at −196°C) of a) Ni(tmtaa)/NaBH₄ (1:100) in diglyme-5% EtOH, b) Ni(tmtaa)/Na-Hg (1:100) in THF, c) Ni(tmtaa)/NaBH(OMe)₃ (1:100) in diglyme-5% EtOH.

Table 3. Reductive Dehalogenation of Bromocyclohexane with NaBH(OMe)₃ and NaBH₃CN Catalyzed by Ni(tmtaa)^{a)}

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

a) Bromocyclohexane = 5.0 × 10⁻¹ mol dm⁻³, bromocyclohexane : NaBH₄ = 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	<i>E</i> _{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 × 10⁻² mol dm⁻³, catalyst : bromocyclohexane : NaBH₄ = 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)/NaBH₄ (Fig. 1a) and Na⁺[Ni^I(tmtaa)]⁻ (Fig. 1b) suggests that some additional ligand coordinates Ni^I in Ni(tmtaa)/NaBH₄. Although the addition of BH₃-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)/NaBH₄. The additional ligand in Ni(tmtaa)/NaBH₄ is not BH₃, but may be H⁻ or BH₄⁻. 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)/NaBH₄ (Fig. 1a). These ESR spectra of the Ni(tmtaa)/NaBH₄ 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.
-