Inorganica Chimica Acta 363 (2010) 3151–3157

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis of {15-benzyloxy-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}nickel(II) perchlorate and its analogs, and their catalytic behavior in reductive debromination of 1-bromo-4-*tert*-butylbenzene

Katsura Mochizuki [a,*], Tomoko Sugita [a], Satoka Kuroiwa [a], Fumi Yamada [a], Kiyoharu Hayano [b], Yasunobu Ohgami [a], Mana Suzuki [a], Syouhei Kato [a]

[a] International Graduate School of Arts and Sciences, Yokohama City University, Yokohama 236-0027, Japan
[b] Hokkaido University of Education Sapporo, Sapporo 002-8502, Japan

ARTICLE INFO

Article history:
Received 19 March 2010
Received in revised form 16 May 2010
Accepted 23 May 2010
Available online 1 June 2010

Keywords:
Nickel complexes
Macrocyclic ligands
Synthesis
Debromination

ABSTRACT

New nickel(II) complexes with macrocyclic ligands bearing benzyloxy [(**5**), (**9**)], 2-methylbenzyloxy (**7**), 3-methylbenzyloxy (**8**), and hydroxy (**6**) groups on the pyridine ring have been synthesized. Structures of the hydroxy substituted macrocyclic ligand (L-OH·3HCl·H_2O), and the benzyloxy substituted ligand (L-OBn·3HCl**)** and its nickel(II) complex (**5**), as well as an analogous Ni(II) complex (**8**), have been revealed by X-ray crystallography. Their catalytic capabilities in the reductive debromination of 1-bromo-4-*tert*-butylbenzene have been elucidated, which has revealed that the pyridine ring can be a suitable position for the introduction of functional groups while maintaining the catalytic capabilities of the nickel(II) complexes.

1. Introduction

Tetraaza macrocyclic metal complexes have been well known to act as catalysts in oxidation and reduction of organic substrates, because of their high resistance to decomposition to relatively higher or lower valence states and the potential coordination of substrates at the apical positions with respect to the macrocyclic plane. It has been reported that some macrocyclic metal complexes catalyze reductive dehalogenation [1] of alkyl [2,3] and aryl halides [4,5]. Macrocyclic Ni(II) complexes containing a pyridine ring in the macrocyclic skeleton have been known to act as catalysts in the reductive debromination of bromoarenes (benzene, naphthalene, and biphenyl derivatives) [4]. In order to design new catalysts for reductive dehalogenation, we plan to introduce another chemical functional group to the nickel(II) complex, e.g., **1**, which is a pyridine-containing macrocycle. For example, connecting a functional group that is a photosensitizer to macrocyclic complexes is expected to facilitate photo-driven catalysis. When introducing a new functional substituent, it is important to know at what position the substituent does not get reduced while maintaining catalytic capability for debromination reactions. The nickel(II) complex **1** has at least two candidates for substituent-introduction positions: the nitrogen atoms of the macrocyclic skeleton and the pyridine ring attached to the skeleton. The introduction of some substituents on the skeletal nitrogen atoms and a number of *N*-functionalized pyridine-containing macrocycles have been reported [6–15], though only a few macrocyclic complexes with substituents on the pyridine ring have been synthesized [16–19]. In this study, we have synthesized nickel(II) complexes with new macrocyclic ligands bearing benzyloxy [(**5**), (**9**)], 2-methylbenzyloxy (**7**), 3-methylbenzyloxy (**8**), and hydroxy (**6**) groups on the pyridine ring of the parent complex (**1**) (Scheme 1). Structures of the hydroxy substituted macrocyclic ligand (L-OH·3HCl·H_2O), and the benzyloxy substituted ligand (L-OBn·3HCl**)** and its nickel(II) complex (**5**), as well as an analogous Ni(II) complex (**8**), have been revealed by X-ray crystallography, The catalytic properties of our synthetic nickel(II) complexes in the reductive debromination of 1-bromo-4-*tert*-butylbenzene are compared with those of some other nickel(II) complexes with *N*-substituted macrocyclic ligands.

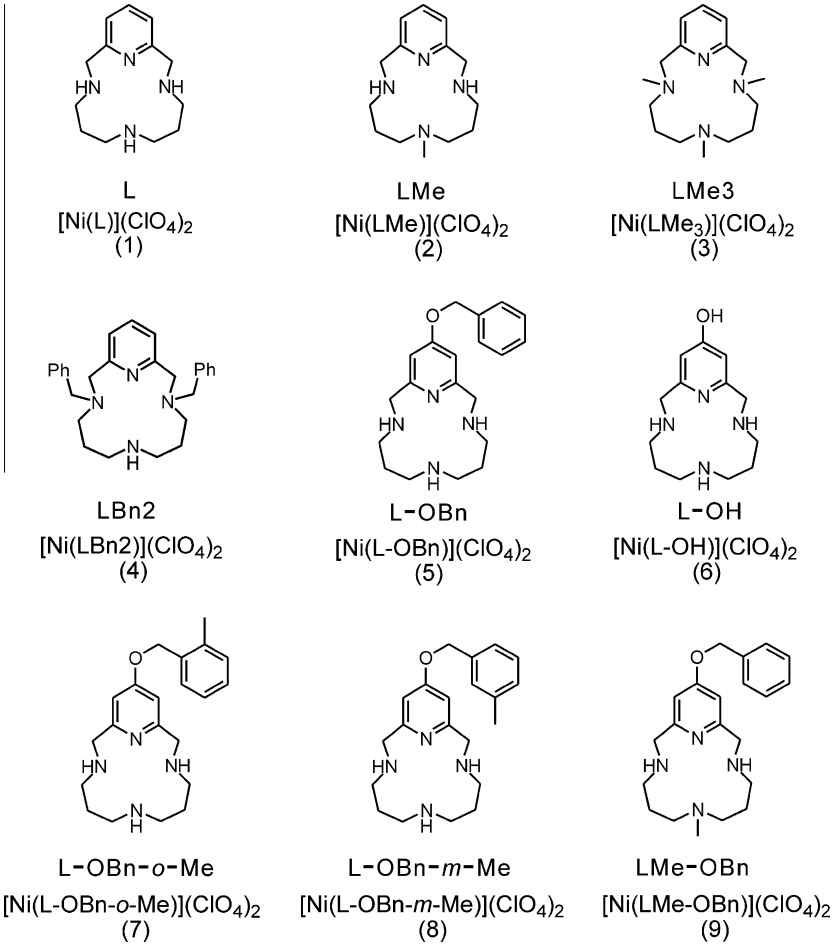
2. Experimental

2.1. Synthesis of ligands and nickel(II) complexes

The nickel(II) complexes, [NiL]$(ClO_4)_2$ (**1**) [6], [Ni(LMe)]$(ClO_4)_2$ (**2**) [7], [Ni(LMe_3)]$(ClO_4)_2$ (**3**) [8], and [Ni(L-Bn_2)]$(ClO_4)_2$ (**4**) [6], were prepared by reported methods. 4-(Benzyloxy)pyridine-2,6-dicarboxaldehyde was synthesized by a modified method reported by Froidevaux et al. [20].

* Corresponding author. Tel.: +81 45 787 2186; fax: +81 45 787 2413.
E-mail address: katsura@yokohama-cu.ac.jp (K. Mochizuki).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.05.051



Scheme 1. Structures of macrocyclic ligands.

2.1.1. 15-Benzyloxy-3,7,11,17-tetraaza-bicyclo[11.3.1]heptadeca-1(17),13,15-triene (L-OBn)

To an ethanol/water (1:1, v/v) solution (40 mL) containing 4-(benzyloxy)pyridine-2,6-dicarboxaldehyde (1.50 g, 6.22 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (1.52 g, 6.29 mmol) was added dropwise an ethanol solution (10 mL) of *N,N*-bis(3-aminopropyl)amine (0.82 g, 6.25 mmol). After the mixture was heated at 60 °C for 6 h, the dark violet solution was evaporated to dryness. The resulting residue was dissolved in 100 mL methanol/water (1:1, v/v) solution, which was cooled to 5 °C, followed by addition of $NaBH_4$ (5.0 g, 132 mmol). The mixture was heated to 60 °C and was stirred for 2 h after further addition of $NaBH_4$ (5.0 g, 132 mmol). The violet solution was acidified to pH 1 by addition of conc. HCl, stirred for 2 h, and neutralized by addition of NaOH. The resulting solution was evaporated to ca. 50 mL and cooled in an ice bath to form white precipitates of boric acid, which were filtered off. NaCl was also removed by precipitation by addition of ethanol to the solution and subsequent filtration. After the ethanolic solution was evaporated to dryness, the resultant residue was dissolved in a minimum amount of water. To the violet solution, addition of $NaClO_4$ yielded precipitates of the perchlorate salt of the copper complex with L-OBn, which was filtered and used for the isolation of free ligand.

The free ligand, L-OBn, was obtained by the removal of copper from the above perchlorate complex using NaCN and further extraction with dichloromethane (yield: 1.59 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.31 (m), 6.62 (s, 2H), 5.07 (s, 2H), 3.79 (s, 4H), 2.70 (*t*, *J* = 5.3 Hz, 4H), 2.58 (t, *J* = 5.4 Hz, 4H), 1.73 (quintet, *J* = 5.3 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.9(t), 46.2(t), 46.9(t), 54.9(t), 70.0(t), 107.8(d), 127.8(d), 128.6(d), 129.0(d), 135.9(s), 161.3(s), 165.5(s). HR-FAB-MS: Found: *m/z* = 341.2342. Calcd for $^{12}C_{20}{}^{1}H_{29}{}^{14}N_4{}^{16}O_1$: *m/z* = 341.2341 $[M+H]^+$.

The hydrochloride salt, L-OBn·3HCl, was obtained from conversion of the free ligand, L-OBn, using hydrochloric acid and a crystal suitable for X-ray analysis was obtained by recrystallization from ethanol/ether (vapor diffusion method).

2.1.2. 15-Hydroxy-3,7,11,17-tetraaza-bicyclo[11.3.1]heptadeca-1(17),13,15-triene (L-OH)

L-OBn·3HCl (0.89 g, 1.98 mmol) was hydrogenated in an aqueous solution containing palladium oxide (0.24 g, 1.96 mmol) as a catalyst under 1 atm hydrogen at room temperature for 24 h. After debenzylation was complete, the catalyst was filtered and the product was isolated by evaporation of the solution (yield: 0.63 g, 84%). Crystals (L-OH·3HCl·H_2O) suitable for X-ray structural analysis were obtained by recrystallization from 1 mol cm^{-3} HCl/ethanol. ^{1}H NMR (300 MHz, D_2O): δ 7.05 (s, 2H), 4.50 (s, 4H), 3.38 (t, *J* = 6.3 Hz, 4H), 3.26 (t, *J* = 7.4 Hz, 4H), 2.35 (quintet, *J* = 6.8 Hz, 4H) ^{13}C NMR (75 MHz, D_2O): δ 21.2(t), 42.5(t), 43.7(t), 49.8(t), 113.0(d), 150.9(s), 166.4(s). HR-FAB-MS: Found: *m/z* = 251.1875. Calcd for $^{12}C_{13}{}^{1}H_{23}{}^{14}N_4{}^{16}O_1$: *m/z* = 251.1872 $[M+H]^+$.

2.1.3. 4-(2-Methylbenzyloxy)pyridine-2,6-dicarboxaldehyde

This was synthesized from the oxidation of 4-(2-methylbenzyloxy)pyridine-2,6-dimethanol, which was prepared by a similar method for 4-(benzyloxy)pyridine-2,6-dimethanol (yield: 89%).

^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0(q), 69.9(t), 111.9(d), 126.2(d), 128.8(d), 129.1(d), 131.0(d), 132.8(s), 137.0(s), 155.0(s), 167.0(s), 192.1(s). FAB mass: *m/z* 256 ([M+H]$^+$). IR (KBr): 1710.7 cm^{-1} ($\nu_{C=O}$).

2.1.4. 15-(2-Methylbenzyloxy)-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L-OBn-o-Me)

The ligand L-OBn-*o*-Me was synthesized by a similar method as that for L-OBn using 4-(2-methylbenzyloxy)pyridine-2,6-dicarboxaldehyde instead of 4-(benzyloxy)pyridine-2,6-dicarboxaldehyde (yield: 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.23 (m), 6.64 (s, 2H), 5.06 (s, 2H), 3.81 (s, 4H), 2.74 (*t*, *J* = 5.6 Hz, 4H), 2.60 (*t*, *J* = 5.7 Hz, 4H), 2.37 (s, 3H), 1.74 (quintet, *J* = 5.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.9(q), 22.5(t), 46.8(t), 47.1(t), 53.0(t), 68.1(t), 107.1(d), 125.5(d), 128.3(2d), 129.8(d), 133.0(s), 136.0(s), 159.8(s), 165.2(s). HR-FAB-MS: Found: *m/z* = 355.2500. Calcd for $^{12}C_{21}{}^1H_{31}{}^{14}N_4{}^{16}O_1$: *m/z* = 355.2498 [M+H]$^+$.

2.1.5. 4-(3-Methylbenzyloxy)pyridine-2,6-dicarboxaldehyde

This was synthesized from the oxidation of 4-(3-methylbenzyloxy)pyridine-2,6-dimethanol, which was prepared by a similar method as 4-(benzyloxy)pyridine-2,6-dimethanol (yield: 79%). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3(q), 70.3(t), 111.9(d), 124.9(d), 128.2(d), 128.8(d), 129.3(d), 134.7(s), 138.6(s), 154.5 (s), 166.9(s), 192.1(d). FAB mass: *m/z* 256 ([M+H]$^+$). IR (KBr): 1703.0 cm^{-1} ($\nu_{C=O}$).

2.1.6. 15-(3-Methylbenzyloxy)-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L-OBn-m-Me)

The ligand L-OBn-*m*-Me was synthesized by a similar method as that for L-OBn using 4-(3-methylbenzyloxy)pyridine-2,6-dicarboxaldehyde (yield: 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.18 (m), 6.62 (s, 2H), 5.04 (s, 2H), 3.79 (s, 4H), 2.73 (*t*, *J* = 5.6 Hz, 4H), 2.58 (*t*, *J* = 5.6 Hz, 4H), 2.38 (s, 3H), 1.73 (quintet, *J* = 5.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3(q), 70.9(t), 111.9(d), 124.9(d), 128.2(d), 128.8(d), 129.3(d), 134.7(s), 138.6(s), 154.5(s), 166.9(s), 192.1(s). HR-FAB-MS: Found: *m/z* = 355.2499. Calcd for $^{12}C_{21}{}^1H_{31}{}^{14}N_4{}^{16}O_1$: *m/z* = 355.2498 [M+H]$^+$.

2.1.7. 15-Benzyloxy-7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (LMe-OBn)

The ligand LMe-OBn was synthesized by a similar method as that for L-OBn using *N,N*-bis(3-aminopropyl)methylamine instead of *N,N*-bis(3-aminopropyl)amine (yield: 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.34 (m), 6.61 (s, 2H), 5.08 (s, 2H), 3.79 (s, 4H), 2.52 (*t*, *J* = 5.6 Hz, 4H), 2.36 (*t*, *J* = 5.7 Hz, 4H), 2.05 (s, 3H), 1.71 (quintet, *J* = 5.7 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9(t), 40.5(q), 46.0(t), 54.2(t), 55.9(t), 69.5(t), 105.7(d), 127.0(d), 127.5(d), 128.0(d), 135.5(s), 160.8(s), 165.0(s). HR-FAB-MS: Found: *m/z* = 355.2496. Calcd for $^{12}C_{21}{}^1H_{31}{}^{14}N_4{}^{16}O_1$: *m/z* = 355.2498 [M+H]$^+$.

2.1.8. [Ni(L-OBn)](ClO$_4$)$_2$ (**5**)

To a methanol solution (10 mL) of L-OBn (0.18 g, 0.54 mmol) was added a methanol solution (10 mL) of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.20 g, 0.54 mmol). After the mixture was heated at 60 °C for 30 min, cooling the methanol solution in an ice bath yielded orange crystals, which were recrystallized from nitromethane/ethyl acetate (vapor diffusion method) (yield: 32%). FAB mass: *m/z* 497 ([M−ClO_4]$^+$). *Anal.* Calc. for $C_{20}H_{28}Cl_2N_4O_9Ni$: C, 40.17; H, 4.72; N, 9.37. Found: C, 40.02; H, 4.70; N, 9.36%.

2.1.9. [Ni(L-OH)](ClO$_4$)$_2$ (**6**)

This complex was synthesized in a similar manner as **5** using L-OH, which had been formed in a neutralized aqueous/methanol solution of L-OH·3HCl·H_2O. Red plate crystals were obtained by slow evaporation of an aqueous solution of the complex containing $NaClO_4$ (yield: 17%). FAB mass: *m/z* 307 ([M−2ClO_4−H]$^+$). *Anal.* Calc. for $C_{13}H_{22}Cl_2N_4O_9Ni$: C, 30.74; H, 4.37; N, 11.03. Found: C, 30.40; H, 4.23; N, 10.92%.

2.1.10. [Ni(L-OBn-o-Me)](ClO$_4$)$_2$ (**7**)

This complex was synthesized in a similar manner as **5** using L-OBn-*o*-Me. Red plate crystals were obtained by recrystallization from nitromethane/ethyl acetate (yield: 56%). FAB mass: *m/z* 511 ([M−ClO_4]$^+$). *Anal.* Calc. for $C_{21}H_{30}Cl_2N_4O_9Ni$: C, 41.21; H, 4.94; N, 9.15. Found: C, 41.04; H, 4.86; N, 9.10%.

2.1.11. [Ni(L-OBn-m-Me)](ClO$_4$)$_2$ (**8**)

This complex was synthesized in a similar manner as **5** using L-OBn-*m*-Me. Crystals suitable for X-ray structural analysis were obtained by recrystallization from nitromethane/ethyl acetate (vapor diffusion method) (yield: 61%). FAB mass: *m/z* 511 ([M−ClO_4]$^+$). *Anal.* Calc. for $C_{21}H_{30}Cl_2N_4O_9Ni$: C, 41.21; H, 4.94; N, 9.15. Found: C, 40.85; H, 4.79; N, 9.10%.

2.1.12. [Ni(LMe-OBn)](ClO$_4$)$_2$ (**9**)

This complex was synthesized in a similar manner as **5** using LMe-OBn. Red needle crystals were obtained by recrystallization from nitromethane/ethyl acetate (yield: 28%). FAB mass: *m/z* 511 ([M−ClO_4]$^+$). *Anal.* Calc. for $C_{21}H_{30}Cl_2N_4O_9Ni$: C, 41.21; H, 4.94; N, 9.15. Found: C, 41.13; H, 4.82; N, 9.17%.

2.2. Physical measurements

Cyclic voltammograms were measured under Ar (99.9999%) with an ALS/chi Electrochemical Analyzer (acetonitrile solutions; potential sweep rate: 0.1 V s^{-1}; Ag/Ag$^+$ reference electrode (BAS RE-5); Pt or glassy-carbon working electrode; Pt counter electrode). Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte.

^{1}H and ^{13}C NMR spectra were recorded with Bruker DRX 300, JEOL FX90Q, and JEOL EPC-400 spectrometers.

Vis-absorption spectra were measured with a Varian Cary 500 scan UV–Vis–NIR spectrophotometer.

2.3. Reductive debromination

To a three-necked 50-mL flask with an Ar inlet tube and a three-way stopcock, the nickel(II) complex [0.04 mmol per nickel(II) ion], $NaBH_4$ (4 mmol), acetonitrile (or diglyme) (2.5 mL), and ethanol (2.5 mL) were added. After the mixture was purged with Ar for 20 min, 1-bromo-4-*tert*-butylbenzene (2 mmol) was added. The reaction mixture was stirred for 3 h at 40 °C. The mixture was filtered and an internal standard (naphthalene) was added to the filtrate, which was analyzed by GC chromatography (internal reference method using authentic samples, Shimadzu GAS chromatograph GC-14A with a chromatopac C-R6A, glass column packed with Thermon-3000 5% SHINCARBON A 60/80).

2.4. Crystallographic studies

X-ray crystallography of single crystals was carried out on a MAC Science MXC3k four-circle (L-OBn·3HCl and **5:** ω-2θ scan; L-OH·3HCl·H_2O and **8:** ω scan) with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). The structures were solved by the direct method (SIR92 and SIR97 [21]), and refined on F^2 by the full-matrix least-squares method SHELXL 97 [22]). The ϕ-scan was applied for absorption correction [23]. All non-hydrogen atoms were refined using anisotropic thermal parameters (riding model refinement). Hydrogen atoms were placed by SHELXL [22]. All calculations were carried out using a Silicon Graphics O_2 work-

Table 1
Crystallographic data of ligands and complexes.

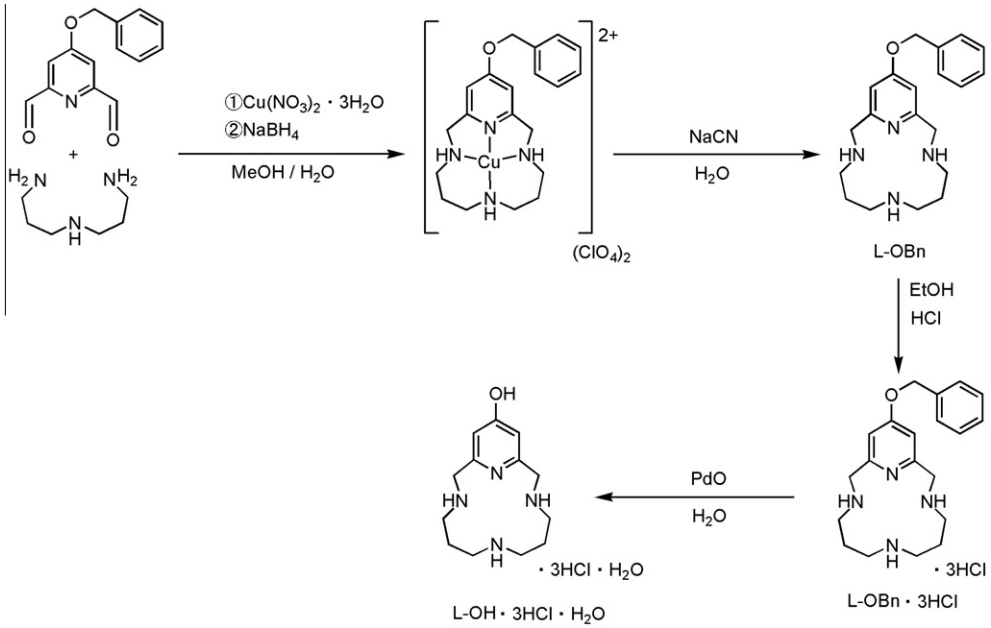
Complex	L-OBn·3HCl	L-OH·3HCl·H_2O	**5**	**8**
Empirical formula	$C_{20}H_{31}Cl_3N_4O_1$	$C_{13}H_2Cl_3N_4O_2$	$C_{20}H_{28}Cl_2N_4Ni_1O_9$	$C_{21}H_{30}Cl_2N_4Ni_1O_9$
Formula weight	449.85	377.74	598.07	904.59
T (K)	298(2)	298(2)	298(2)	298(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pbca*	$P2_1$	*Pbca*
a (Å)	11.599(14)	16.016(4)	14.091(3)	30.598(13)
b (Å)	7.181(4)	11.789(5)	10.027(2)	19.259(11)
c (Å)	29.343(6)	19.994(3)	19.153(5)	8.816(3)
β (°)	105.78(4)	–	109.953(18)	–
V (Å^3)	2352(3)	3775(2)	2543.9(10)	5194(4)
Z	4	8	4	8
D_{cacl} (Mg m^{-3})	1.270	1.329	1.562	1.565
μ (mm^{-1})	0.407	0.497	1.029	1.010
F(0 0 0)	952	1656	1240	2544
Crystal size (mm)	0.80 × 0.80 × 0.20	0.60 × 0.15 × 0.15	0.85 × 0.10 × 0.10	1.00 × 0.50 × 0.15
Reflections collected	5680	4841	6354	6680
Independent reflections	5416 [$R_{(int)}$ = 0.0093]	4334 [$R_{(int)}$ = 0.0012]	6175 [$R_{(int)}$ = 0.0904]	5983 [$R_{(int)}$ = 0.0467]
Goodness-of-fit	1.011	1.016	0.976	1.013
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0770, wR_2 = 0.1729	R_1 = 0.0709, wR_2 = 0.1240	R_1 = 0.0832, wR_2 = 0.1718	R_1 = 0.0869, wR_2 = 0.2353
Largest diff. peak and hole (e Å^3)	0.991 and −0.591	0.282 and −0.302	0.469 and −0.394	0.638 and −0.414

station (MaXus program system provided by MAC Science). Structural diagrams were drawn using ORTEP-3 for Windows [24]. Crystallographic data for the complexes are listed in Table 1. During the calculations, no restraints were applied for L-OBn·3HCl, L-OH·3HCl·H_2O, and **8**, whereas, in the case of **5**, two phenyl groups comprised of C(15), C(16), C(17), C(18), C(19), and C(20), and C(35), C(36), C(37), C(38), C(39), and C(40) were restrained so as to maintain an ideal hexagon by the SHELXL command, AFIX66 and AFIX65 (data/restraints/parameters: 6175/1/643).

3. Results and discussion

The synthetic route for the macrocyclic ligands with a substituent on the pyridine ring is shown in Scheme 2. The target ligand, L-OBn, with a benzyloxy substituent at the 4th position of the pyridine ring of L was synthesized via the 1:1 condensation reaction between 4-(benzyloxy)pyridine-2,6-dicarboxaldehyde and *N,N*-bis(3-aminopropyl)amine using copper(II) ion as a template. Analogous ligands were synthesized by this method as well. The nickel complexes were synthesized by direct complex formation between isolated ligands and nickel(II) ions in methanolic solutions. Significantly, the synthesis of L-OBn also led to the isolation of the ligand L-OH, which was prepared from debenzylation of L-OBn·3HCl by hydrogenation with PdO. The debenzylation process did not proceed for the free ligand L-OBn but succeeded only for the hydrochloride salt L-OBn·3HCl. The ligand with the OH group on the pyridine ring, L-OH, enabled us to synthesize a new type of macrocyclic compound having Ru(bpy)$_3$ as a photosensitizer [25] and new bis(macrocyclic) ligands linked at the pyridine rings [26].

The crystallographic data for the ligands and two Ni(II) complexes are shown in Table 1. The ligand L-OBn was crystallized as a hydrochloride salt, L-OBn·3HCl, which allowed X-ray structural



Scheme 2. Synthesis of ligands.

analysis (Fig. 1a). The macrocyclic skeleton folded along the axis penetrating N(3) and N(11). The angle between the pyridine ring and the mean plane consisting of N(3), N(7), and N(11) in the macrocyclic skeleton was ca. 54°. Furthermore, the benzyl group was extended with its phenyl group twisting at ca. 71° against the pyridine ring of the macrocycle. The three imino nitrogens were protonated to result in a hydrogen bonding network spread through three chloride anions[1].

The X-ray structural analysis of L-OH·3HCl·H_2O clearly showed the success of the debenzylation (Fig. 1b). The angle between the pyridine ring and the mean plane consisting of N(6), N(10), and N(14) in the macrocyclic skeleton was ca. 72°. The folding of the macrocyclic skeleton was larger than that of the benzyl-substituted one, L-OBn·3HCl. In this case, the hydroxy group, one molecule of water, and the three protonated nitrogens were joined to form a hydrogen bonding network[2].

The crystal of [Ni(L-OBn)]$(ClO_4)_2$ obtained from recrystallization in nitromethane/ethyl acetate contained two forms with different conformations around the benzyl groups (Fig. 2). One macrocyclic complex containing Ni(2) took a nearly planar form, where the angle between the phenyl ring of the benzyl group and the mean plane consisting of N(5), N(6), N(7), and N(8) was ca. 22°. In the other macrocyclic complex containing Ni(1), the phenyl ring of the benzyl group was nearly perpendicular to the macrocyclic N4-plane; the angle between the phenyl ring and the mean plane consisting of N(1), N(2), N(3), and N(4) was ca. 88°. The macrocyclic skeleton took almost the same form in each macrocyclic nickel(II) complex. Two nickel(II) ions adopted a square planar conformation with three imino protons lying in the same direction against the N4-plane in both macrocyclic nickel(II) complexes. The average Ni–N distances were ca. 1.93 and 1.92 Å for Ni(1) and Ni(2), respectively. These values are typical for low-spin square planar macrocyclic Ni(II) complexes. Perchlorates did not coordinate to the nickel(II) ions, though some of them likely interacted with imines by hydrogen bonds [O(5)–N(3): 3.029; O(4)–N(2): 3.134 Å].

In contrast to the above mentioned [Ni(L-OBn)]$(ClO_4)_2$, the crystal of [Ni(L-*m*-MeOBn)]$(ClO_4)_2$, which has a methyl group on the phenyl ring, adopted a unique form of the complex (Fig. 3). Although the macrocyclic skeleton was very similar to that of [Ni(L-OBn)]$(ClO_4)_2$, the benzyl group extended from the macrocyclic part with ca. 55° of a twisted angle between the phenyl ring and the mean N4-plane consisting of N(3), N(7), N(11), and N(17). The nickel(II) ion adopted a typical four-coordinate square planar conformation, enclosed with four nitrogen donors which were almost in the same plane (average Ni–N distance: ca. 1.91 Å).

The VIS-absorption data for the synthesized complexes are listed in Table 2. In solid state and in nitromethane solution, all the complex perchlorates showed only one intense absorption band around 450–480 nm, indicating that these nickel complexes are in a square planar coordination geometry. On the other hand, in acetonitrile solutions, these Ni(II) complexes showed at least two bands, one of which appeared around 450–460 nm which was attributed to a four-coordinate square planar species and one around 720–750 nm which was attributed to a six-coordinate species. These results suggest that the Ni(II) complexes are in equilibrium between a four-coordinate species and a solvent coordinated six-coordinate species in acetonitrile solution. Similar

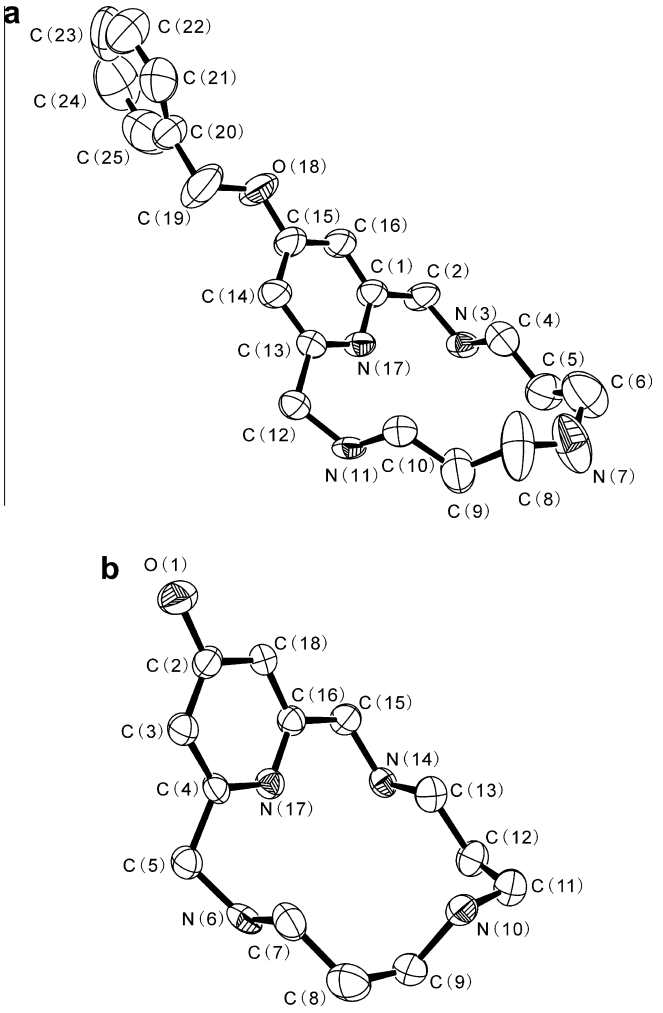


Fig. 1. Ortep drawings of the cationic portions of L-OBn·3HCl (a) and L-OH·3HCl·H_2O (b) with 50% probability thermal ellipsoids.

phenomena have been observed for analogous macrocyclic Ni(II) complexes [26,27].

Cyclic voltammograms for the nickel(II) complexes showed two reversible waves of which $E_{1/2}$ ranged from +0.77 V to +0.9 V and between −1.5 V and −1.59 V. These may be assignable to the Ni^{II}/Ni^{III} and Ni^{I}/Ni^{II} redox processes, respectively (Table 3). The $E_{1/2}$ of Ni^{I}/Ni^{II} for the *N*-methylated complex, **9**, was −1.509, which was slightly (ca. 80 mV) more positive than those for the other non-methylated complexes, **5**–**8**, as well as that for $E_{1/2}$ of Ni^{II}/Ni^{III}. This difference in the redox behavior may play a role in differentiating complex **9** from other complexes in catalytic capability for the following debromination reactions.

Debromination of 4-bromo-*tert*-buthylbenzene mediated by macrocyclic nickel(II) complexes was carried out at 40 °C for 3 h with a reactant ratio of Ni(II):substrate:$NaBH_4$ = 1:50:100. The conversion yields, ranging from 14% to 63%, are shown in Table 4. The debromination proceeded only when macrocyclic nickel(II) complexes co-existed in the reaction solution. It was found that the introduction of methyl groups to the nitrogen atoms of the macrocyclic skeleton reduced the catalytic activity. The conversion yield by complex **2**, which had one methyl group on the nitrogen at the 7th position, was 26%, which was significantly lower than that of the parent complex **1** (85%). A similar decrease in catalytic capability by the introduction of a methyl group was found for the synthetic benzyloxy substituted complexes (**5**: 92%; **9**: 10%). Further

[1] The selected distances are as follows: Cl(1)–N(3): 3.24, Cl(1)–N(11): 3.20, Cl(1)–N(11#1): 3.12, Cl(2)–N(3#2): 3.02, Cl(3)–N(7): 3.28, and Cl(3)–N(7#1): 3.03 Å (symmetry operations: #1: $(2-x, -1/2+y, 1.5-z)$, #2: $(x, 1+y, z)$).

[2] The selected distances are as follows: O(1)–Cl(21#1): 2.99, Cl(19)–N(10): 3.18, Cl(19)–N(14#2): 3.21, Cl(19)–N(6#2): 3.17, Cl(20)–N(10): 3.09, Cl(20)–O(22#3): 3.13, Cl(21)–N(6#2): 3.10, Cl(21)–O(22#4): 3.07, and O(22)–N(14#2): 2.73 Å (symmetry operations: #1: $(1/2+x, y, 1/2-z)$, #2: $(1.5-x, -1/2+y, z)$, #3: $(-1/2+x, -1/2-y, -z)$, #4: $(x, -1/2-y, 1/2+z)$).

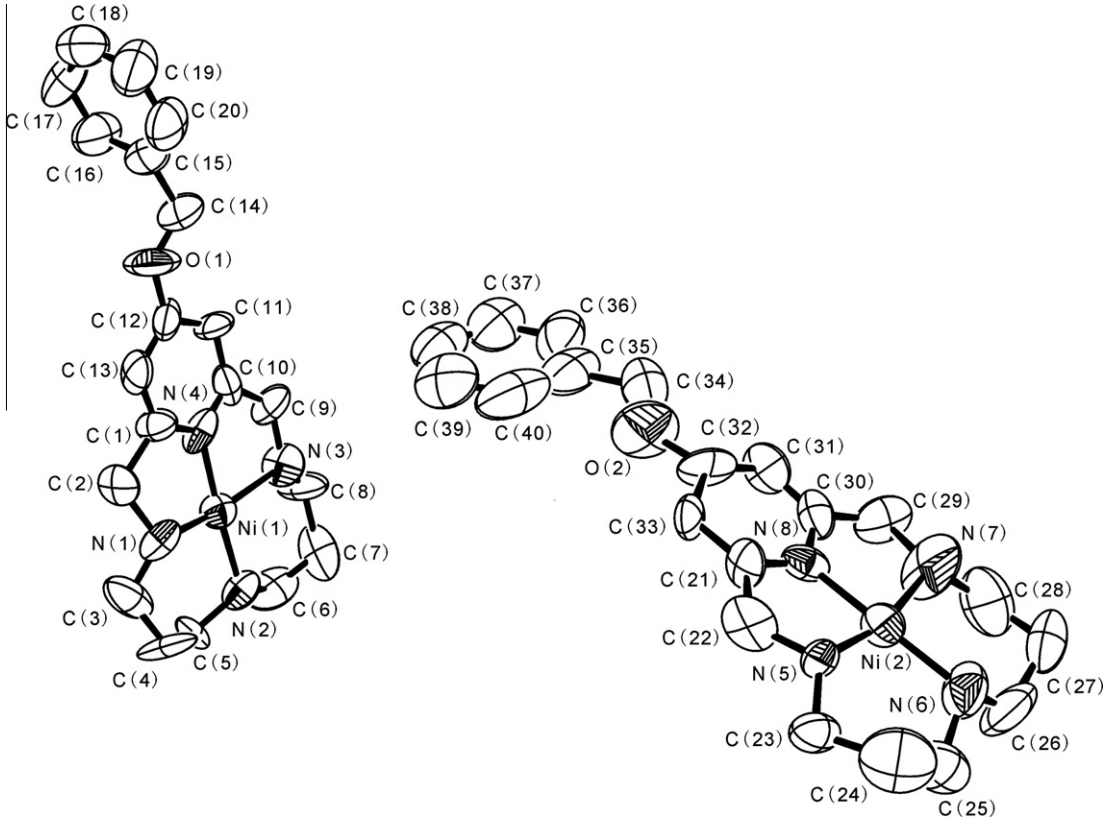


Fig. 2. Ortep drawings of the cationic portions of $[Ni(L\text{-}OBn)](ClO_4)_2$ with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): N(1)–Ni(1) 1.91(3), N(2)–Ni(1) 1.964(11), N(3)–Ni(1) 1.99(3), N(4)–Ni(1) 1.878(13), N(5)–Ni(2) 1.97(2), N(6)–Ni(2) 1.910(16), N(7)–Ni(2) 1.93(4), N(8)–Ni(2) 1.851(13), N(4)–Ni(1)–N(1) 89.0(12), N(1)–Ni(1)–N(2) 95.2(14), N(4)–Ni(1)–N(3) 78.3(13), N(2)–Ni(1)–N(3) 97.5(15), N(8)–Ni(2)–N(7) 83.4(17), N(6)–Ni(2)–N(7) 96.4(19), N(8)–Ni(2)–N(5) 83.7(12), N(6)–Ni(2)–N(5) 96.5(15).

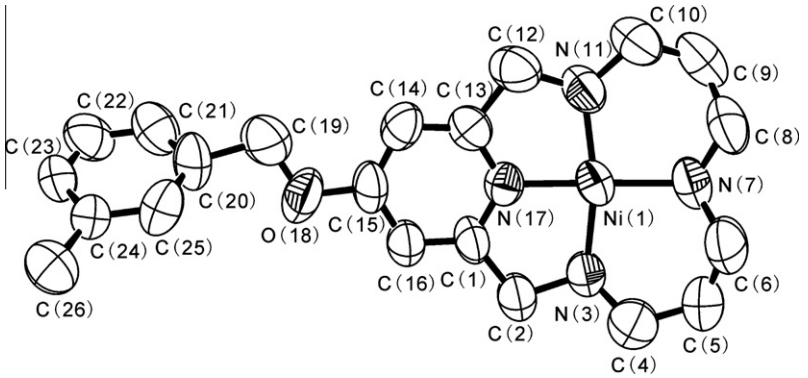


Fig. 3. Ortep drawing of the cationic portions of $[Ni(L\text{-}m\text{-}MeOBn)](ClO_4)_2$ with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Ni(1)–N(17) 1.841(6), Ni(1)–N(11) 1.907(8), Ni(1)–N(3) 1.922(7), Ni(1)–N(7) 1.953(7), N(17)–Ni(1)–N(11) 83.6(3), N(17)–Ni(1)–N(3) 84.2(3), N(11)–Ni(1)–N(7) 97.2(3), N(3)–Ni(1)–N(7) 94.9(3).

Table 2
Vis-absorption spectral data.

λ_{max} (nm) (ε/mol^{-1} dm^3 cm^{-1})			
Complex[a]	Solid	Nitromethane	Acetonitrile
5	471	464(160)	725(14), 465(63), 329(shoulder)
6	463	462(170)	725(14), 467(67), 330(shoulder)
7	459	461(190)	748(11), 459(78), 330(shoulder)
8	467	462(178)	726(15), 458(79), 330(shoulder)
9	470	466(180)	727(16), 468(74), 340(shoulder)

[a] [Complex]: 3.0×10^{-3} mol dm^{-3}, 25 °C.

introduction of two methyl groups to complex **2** led to complex **3**, for which the conversion yield was even further decreased (16%). The introduction of the more bulky benzyl groups drastically decreased the conversion yield (**4**: 2%). In contrast to the introduction of substituents on the nitrogen atoms, the introduction of substituents to the 4th position of the pyridine ring did not greatly reduce the catalytic activity of this type of nickel(II) complex. Conversion yields were as follows: **5** (benzyloxy): 95%; **6** (hydroxy): 78%; **7** (2-methylbenzyloxy): 72%; and **8** (3-methylbenzyloxy): 82%.

In conclusion, new nickel(II) complexes with macrocyclic ligands bearing benzyloxy [(**5**), (**9**)], 2-methylbenzyloxy (**7**), 3-methylbenzyloxy (**8**), and hydroxy (**6**) groups on the pyridine ring have been synthesized. Their catalytic properties in the reductive debromination of 1-bromo-4-*tert*-butylbenzene revealed that the pyridine ring can be a suitable position for the introduction of new

Table 3
Cyclic voltammetric data for Ni(II) complexes.[a]

Complex	E_{pc}/V	E_{pa}/V	$E_{1/2}$/V	δE_p/V
5	+0.745	+0.832	+0.789	0.087
	−1.642	−1.530	−1.586	0.112
6	+0.747	+0.885	+0.816	0.138
	−1.651[b]	−1.526	−1.589	0.125
7	+0.728	+0.824	+0.776	0.096
	−1.656	−1.527	−1.592	0.129
8	+0.743	+0.832	+0.788	0.084
	−1.634	−1.539	−1.587	0.095
9	+0.840	+0.942	+0.891	0.102
	−1.549	−1.468	−1.509	0.081

[a] Values are normalized to *vs.* Fc/Fc^+. Measurement condition: [electrolyte] = 0.1 mol dm^{-3} tetraethylammonium perchlorate. Potential sweep rate 0.1 V s^{81}. [Complex] = 3×10^{-3} mol dm^{-3} in acetonitrile, 25 °C.
[b] A pre-wave appeared at −1.202 V.

Table 4
Debromination of 1-bromo-4-*t*-butylbenzene.[a]

Complex	Conversion (%)[b]
1	85
2	26[c]
3	16[c]
4	2[c]
5	95
6	78
7	72
8	82
9	10

[a] Ni(II) complex: 0.04 mmol, substrate: 2 mmol, $NaBH_4$: 4 mmol, Solvent: acetonitrile/EtOH = 1:1 (V/V), 40 °C, 3 h.
[b] GC conversion yield.
[c] Solvent: diglyme/EtOH = 1:1 (V/V).

functional groups, while maintaining the catalytic capabilities of the nickel(II) complexes.

Acknowledgment

This work was partially supported by JSP Grant-in-Aid for Scientific Research (C) 20550139.

Appendix A. Supplementary material

CCDC 769766, 769767, 769768 and 76769 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.05.051.

References

[1] F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 102 (2002) 4009.
[2] A.M. Stolzenberg, Z. Zhang, Inorg. Chem. 36 (1997) 593.
[3] T. Arai, K. Kashitani, H. Kondo, S. Sakaki, Bull. Chem. Soc. Jpn. 67 (1994) 705.
[4] M. Stiles, J. Org. Chem. 59 (1994) 5381.
[5] K. Mochizuki, T. Sugita, F. Yamada, N. Mochizuki, K. Hayano, Y. Ohgami, Inorg. Chim. Acta 362 (2009) 1204.
[6] N.W. Alcock, K.P. Balakrishnan, P. Moore, G.A. Pike, J. Chem. Soc., Dalton Trans. (1987) 889.
[7] J. Costa, R. Delgado, Inorg. Chem. 32 (1993) 5257.
[8] N.W. Alcock, P. Moore, H.A.A. Omar, J. Chem. Soc., Dalton Trans. (1987) 1107.
[9] K.P. Guerra, R. Delgado, M.G.B. Drew, V. Félix, Dalton Trans. (2006) 4124.
[10] K.P. Guerra, R. Delgado, L.M.P. Lima, M.G.B. Drew, V. Félix, Dalton Trans. (2004) 1812.
[11] F. Dioury, I. Sylvestre, J.-M. Siaugue, V. Wintgens, C. Ferroud, A.F. Réguillon, J. Foos, A. Guy, Eur. J. Org. Chem. (2004) 4424.
[12] X. Cui, M.J. Calhorda, P.J. Costa, R. Delgado, M.G.B. Drew, V. Félix, Helv. Chim. Acta 87 (2004) 2613.
[13] S. Autzen, H.-G. Korth, R. Boese, H.D. Groot, R. Sustmann, Eur. J. Inorg. Chem. (2003) 1401.
[14] V. Félix, M.J. Calhorda, J. Costa, R. Delgado, C. Brito, M.T. Duarte, T. Arcos, M.G.B. Drew, J. Chem. Soc., Dalton Trans. (1996) 4543.
[15] N.W. Alcock, K.P. Balakrishnan, A. Berry, P. Moore, C.J. Reader, J. Chem. Soc., Dalton Trans. (1988) 1089.
[16] H. Takalo, J. Kankare, J. Heterocycl. Chem. 27 (1990) 167.
[17] R. Breslow, S. Singh, Bioorg. Chem. 16 (1988) 408.
[18] U. Lüning, W. Hacker, J. Prakt. Chem. 341 (1999) 662.
[19] U. Lüning, M. Gerst, J. Prakt. Chem. 334 (1992) 656.
[20] P. Froidevaux, J.M. Harrowfield, A.N. Sobolev, Inorg. Chem. 39 (2000) 4678.
[21] A. Altomare, G. Cascarno, C. Giacovazzo, A. Gualiardi, J. Appl. Crystallogr. 27 (1994) 435.
[22] G. M. Sheldrick, University of Göttingen, Germany, 1997.
[23] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., Sect A 24 (1968) 351.
[24] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[25] Y. Takahashi, M. Suzuki, S. Hayano, K. Mochizuki, in: The 57st Symposium on Coordination Chemistry of Japan, Nagoya, 2007, p. 289 (Abstract (2PA-053) Details will be reported elsewhere).
[26] K. Mochizuki, M. Fujimoto, H. Ito, T. Ito, Bull. Chem. Soc. Jpn. 53 (1980) 2535.
[27] K. Mochizuki, Y. Ikeda, Bull. Chem. Soc. Jpn. 63 (1990) 1587.