Functional Porphyrins as Receptor Models

Hisanobu Ogoshi and Tadashi Mizutani

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering,
Kyoto University, [REDACTED]

Abstract: A series of functionalized porphyrins were prepared to show their potential for the models of various types of receptors. Atropisomerization was controlled by the combination of meso substituents and β -substituents. Chiral porphyrins were also prepared according to several different approaches. Molecular recognition functions of these functional porphyrins are also described. Perfluoroalkylporphyrins showed characteristic oxidation potential and can serve as a ^{19}F NMR probe. They are applied to a novel catalyst and to the study of heme-protein interactions.

1. Introduction

Metal complexes of porphyrins and related nitrogen macrocycles perform a number of important functions to maintain diverse biological processes such as photosynthesis, metabolism, biosynthesis and oxygen transport. In biochemistry, these porphyrins are recognized by proteins to tune their functions in the porphyrin-protein complex. In chemistry, however, we can use porphyrin as a host recognizing guest molecules. The rigid framework of porphyrins is ideal as the basic unit structure for the host molecule, on which various recognition groups with different interaction nature are fixed. Various spectroscopic methods available for the analysis of porphyrin provide powerful tools to study host-guest complex formation. A number of spectroscopic techniques such as NMR, UV-vis, circular dichroism, magnetic circular dichroism, fluorescence, IR, and Raman have been successfully used to obtain structural information. Porphyrin has four different sites for functionalization: (1) central metal, (2) meso-position, (3) pyrrole β -position, and (4) pyrrole nitrogen. Site specific functionalization can be achieved by careful design of the synthetic route. In this paper, we report the various attempts to introduce the desired recognition groups into the porphyrin framework, to construct unique functional porphyrins and functional metalloporphyrins.

Figure 1. Four functional sites of porphyrin.

2. Synthesis of Multi-functional Porphyrin

To functionalize porphyrins, the first strapped porphyrin was reported independently by Ogoshi (1, ref. 1) and Battersby (ref. 2). By changing the length of the strap, the porphyrin was able to distinguish the bulkiness of the axial ligands and to regulate the spin state of the ferric complex.

Functionalization at the meso-position seems to be advantageous for construction of a convergent array of recognition groups above the porphyrin plane. Particularly, aromatic rings at the meso-position are perpendicular to the porphyrin plane, so that the recognition groups attached to the aromatic ring will be fixed above the porphyrin plane. Several functional porphyrins have been prepared along this line.

5,15-Diarylporphyrin (**3**) was prepared by the condensation of appropriate dipyrromethane and aldehyde (ref. 3). The condensation reaction conditions should not be too vigorous because cleavage of the aryl-porphyrin bond occurs. For example, reflux in propionic acid gave the monoarylporphyrin (**4**) as the major product. By using an

Figure 2. Binding of leucine methyl ester to the bifunctional Rh porphyrin.

aromatic aldehyde having recognition groups, the recognition groups can be fixed on the porphyrin plane. Owing to the atropisomerism, trans and cis isomers form when unsymmetrical aromatic aldehyde is used. The fluctuation of the aryl group will affect the binding properties of the porphyrin host. Control of the rotation of the aryl groups along the single bond connecting the aryl group to porphyrin, which is called atropisomerization, is important from the viewpoint of host design. Introduction of ethyl groups to the β -position of pyrrole of **3** ($R = 1$ -naphthyl) prevents the atropisomerization. The careful design of combinations of meso-substituents and β -substituents thus successfully controls the isomerization and fluctuation of the recognition groups on the meso-aromatic ring.

To construct a receptor for amino acid esters, the rhodium complex of *trans*-5,15-bis(2-hydroxynaphthyl)porphyrin (**6•Rh**) was prepared (ref. 4) (Figure 2). The binding constants were quite large in CHCl_3 due to the strong coordinating interaction between the trivalent rhodium ion and the amino groups. Coordination of the acetone enolate anion to the rhodium weakened the interaction, and the binding constants fell in the measurable range by the UV-vis spectroscopic titrations. With this two-point recognition system, where a strong coordinating interaction and a weak hydrogen bonding interaction operate, precise evaluation of the hydrogen bonding interaction was still difficult. To overcome this difficulty, the zinc complex of the same porphyrin (**6•Zn**) was then studied as the host (Figure 3). The binding constants for amines and amino acid esters are 1700 – $11\,000\text{ M}^{-1}$; the smaller binding constants are highly suitable for the study of subtle intermolecular interactions like hydrogen bonding.

The binding of amino acid esters was systematically studied by use of the zinc porphyrin (**6•Zn**) (ref. 5). In this study, we prepared the porphyrins with some of the recognition groups blocked by the alkyl group or replaced with hydrogen. These reference porphyrins provide good evidence for the interaction mode of the host-guest complex. First, the binding constants of the reference porphyrin (**7**) are reduced, indicating that the hydroxyl groups of **6•Zn** do assist the complex

Figure 3. Binding of leucine methyl ester to the bifunctional Zn porphyrin (left). Binding of aspartic acid dimethyl ester to the trifunctional Zn porphyrin.

formation. Comparison of the binding constants revealed the contribution of a particular recognition group to the overall free energy change. Second, the porphyrin (**6•Zn**) and its reference porphyrin (**7**) showed completely different spectroscopic behavior in the circular dichroism spectra. The two-point interaction between host and guest, one coordinating interaction and one hydrogen bonding interaction, was probed by the complexation-induced circular dichroism spectroscopy. Only the host-guest combinations, which are able to interact with each other in a bidentate fashion, showed split-type induced circular dichroism in the Soret band (ref. 6).

Several 5,15-diarylporphyrins were designed to bind quinones (ref. 7), amino acid esters with polar side chains (Figure 3, right) (ref. 8) and carbohydrate derivatives (ref. 9). *cis*-5,15-Bisquinolymporphyrin zinc complex (**5•Zn**) shows a marked affinity for glucose derivatives in CHCl_3 , indicating that this series of porphyrin receptors are also applicable to the recognition of a complex guest like sugars. The host **8•Zn** has three recognition groups which are complementary to dimethyl aspartate. Enthalpic and entropic contributions to the recognition were determined by these multi-point recognition hosts. As the number of recognition groups increases, the entropic change increases negatively, showing that the host-guest complex becomes ordered. The effects of recognition groups of **6•Zn** and **8•Zn** on the rates of complex formation were also examined by ^1H NMR relaxation time

studies (ref. 10). The hydrogen bonding accelerates the host-guest complex formation, without affecting the dissociation rate.

5,10,15,20-Tetraarylporphyrins were prepared by condensation of pyrrole with appropriate aromatic aldehydes. The $\alpha,\alpha,\alpha,\alpha$ -atropisomer of **11** has four hydrogen bonding donor groups convergently arranged above the porphyrin plane. This porphyrin (**11**) was able to bind quinones selectively via four hydrogen bonding interactions (ref. 11). The binding constants were in the range 30 (for quinone)–20 000 M^{-1} (for 2,3,5,6-tetramethoxyquinone) at 15 °C in CHCl_3 . For the latter guest, four simultaneous hydrogen bonds stabilize the complex as proved by the X-ray crystallographic study. It is noteworthy that **11** undergoes no detectable atropisomerization after being refluxed for 2 h in toluene, although this porphyrin has no alkyl groups on the β -position of pyrrole. Therefore, four naphthyl groups at the meso-position cooperatively inhibit the atropisomerization, which presumably proceeds via a puckered transition state. This observation suggests that the atropisomerization is not a matter of a local bond rotation, but deformation of the whole porphyrin plane.

Atropisomerization was used to investigate the induced fit-type host-guest complexation. The atropisomerization of tetrakis(2-hydroxyphenyl)porphyrin (**13**) was triggered by the addition of quinones (ref. 12). After sufficient time, about 80 % of **13** was isomerized to the $\alpha,\alpha,\alpha,\alpha$ -atropisomer at 25 °C in CDCl_3 in the presence of 10 equivalents of tetramethoxy-*p*-benzoquinone. In an independent experiment, it was shown that tetramethoxy-*p*-benzoquinone is bound by $\alpha,\alpha,\alpha,\alpha$ -isomer of **13** with a binding constant of 6000 M^{-1} , while it is bound by $\alpha,\alpha,\alpha,\beta$ -isomer of **13** with a binding constant of only 300 M^{-1} . Therefore, the high affinity of the guest to the $\alpha,\alpha,\alpha,\alpha$ -isomer induced the atropisomerization of the host. The four long alkyl groups of **13** were attached to the phenyl groups to improve the poor solubility of this porphyrin. This modification dramatically improved the solubility of **13** in usual organic solvents.

Tetrakis(2-carboxyphenyl)porphyrin (**14**) with nonyl groups at para position forms a dimer, the formation of which induces the atropisomerization to the $\alpha,\alpha,\alpha,\alpha$ -isomer. In CHCl_3 , $\text{CHCl}_2\text{CHCl}_2$, and CCl_4 at 80 °C, 95–99 % of **14** becomes the $\alpha,\alpha,\alpha,\alpha$ -isomer eventually (ref. 13). The equilibrium constant for the dimer formation at 80 °C in $\text{CHCl}_2\text{CHCl}_2$ was estimated to be $7.4 \times 10^7 \text{ M}^{-1}$. Introduction of alkyl groups again improved the solubility of **14**.

The functionalization at the meso-position was further studied and improved by C. K. Chang (ref. 14) and K. Maruyama (ref. 15), and has made contributions to the progress of the model systems of the photosynthetic reaction center.

3. Intrinsic Chiral Porphyrins with C_2 Symmetry

Several chiral porphyrins with C_2 symmetry have been designed and synthesized (**15**–**19**, Fig. 4). For chiral recognition, three recognition groups with varying nature of recognition forces should be fixed above the porphyrin plane to form the chiral recognition pocket. The syntheses were made possible via appropriate selection of pyrrole units and control of the atropisomerization of the meso-substituents. The porphyrin (**18**) has three recognition groups, zinc, hydroxyl and carbomethoxy groups, which are complementary to the structure of amino acid derivatives. The porphyrin (**19**) has zinc, NH, and aromatic groups, which can also recognize amino acid derivatives.

The first intrinsic chiral porphyrin with C_2 symmetry (**15**) was prepared by the Vilsmeier reaction of the nickel complex of **6** (ref. 16). The enantiomers were separated by use of high pressure liquid chromatography on cellulose tris(3,5-dimethylphenylcarbamate) after converting them to the tribenzyl derivatives (**20**).

Chiral porphyrin having a similar arrangement of substituents but improved recognition capability (**18**) was prepared by a stepwise synthesis (ref. 17). Coupling of two dipyrromethanes afforded the C_2 symmetric porphyrin (**18**). Two enantiomers were resolved by HPLC chiral column. This chiral porphyrin can discriminate the chirality of amino acid esters in CHCl_3 . At 15 °C, **18** bind L-valine methyl ester with the binding constant of 6130 M^{-1} and D-valine methyl ester with 2440 M^{-1} . Host **18** showed preference for L-amino acid esters consistently except for serine benzyl ester. For serine benzyl ester, the chiral preference was reversed, i.e., **18** preferred D-serine benzyl ester. This behavior can be reasonably explained by the interaction between the side chain group of amino acid esters and the carbomethoxy group of the host. The interaction is attractive for serine benzyl ester, while it is repulsive for other amino acid esters. This conclusion was verified by comparing the binding affinity of **18** with those of the reference porphyrins. Comparison of binding constants indicated that

the carbomethoxy group assisted the binding of serine benzyl ester, whereas it disturbed the binding of other amino acid esters.

Figure 4. Chiral porphyrins with C_2 symmetry. The C_2 axes are shown by arrows.

Another strategy for the synthesis of intrinsic chiral porphyrin with C_2 symmetry is to start from $\alpha,\alpha,\beta,\beta$ -tetrakis(2-aminophenyl)porphyrin (**24**). Double bridging reaction with unsymmetrical bifunctional reagent afforded meso-porphyrin and a pair of chiral porphyrin (ref.18). The synthesis is much simpler than that of the chiral porphyrin **18**. The meta-phenylene bridged porphyrin (**19**) has a

good binding pocket for amino acid esters. This porphyrin (**19**) showed enantioselective binding of amino acid esters. For the binding of valine methyl ester in CHCl_3 at 15°C , the binding constant of one enantiomer of **19** is $22\,000\text{ M}^{-1}$ while that of the other enantiomer is 3900 M^{-1} . The para-phenylene bridged porphyrins (**25**) has a shallow binding pocket and the binding of amino acid esters was very weak. The binding constant of **25** for phenylalanine methyl ester was 900 M^{-1} (CHCl_3 at 15°C) while that of **19** was $15\,000\text{ M}^{-1}$. ^1H NMR of the **19**-guest system revealed an interesting feature of the complexation. The NH_2 protons and $\alpha\text{-CH}$ proton of L-valine methyl ester in the complex appeared at -4.57 and -2.90 ppm, respectively, in CD_2Cl_2 at 301 K . Compared to the free guest, the complexation induced shifts amount to -6.04 and -6.21 ppm, respectively. These large upfield shifts are ascribed to the fixation of guest just above the porphyrin plane, where the ring current effects are very strong.

Another type of chiral porphyrin, 5,10-diarylporphyrin (**16**), was prepared by a stepwise propagation of the pyrrole unit (ref. 19), although the yield was low. The trans isomer is chiral. This porphyrin also has C_2 symmetry axis, which lies along the N-Zn-N line. Protoheme-type chiral porphyrin (**17**) was also prepared (ref. 20). However, the methoxycarbonyl groups are too far from the porphyrin plane to construct a convergent recognition pocket.

The fourth functional site of porphyrin, the pyrrole nitrogen, can be alkylated by a usual alkylation reagent. Alkylation of the nitrogen alters a number of properties of porphyrin: (1) The porphyrin plane becomes deformed. (2) The alkylated nitrogen becomes more basic. (3) The complex with divalent metal is cationic. Chiral *N*-alkylporphyrin was reported, whose absolute stereochemistry has been determined by X-ray crystallographic diffraction studies (ref. 21). Inoue et al. prepared the chiral strapped porphyrin and applied it to the asymmetric oxygenation of olefins (ref. 22).

Dimeric chiral porphyrin with C_2 symmetry has been prepared by Crossley et. al (ref. 23). Condensation of β -aminoporphyrin with formaldehyde afforded a Tröger's base-type porphyrin dimer. The dizinc complex of the porphyrin showed a marked enantioselectivity for histidine esters (80–86 % e.e.) and lysine benzyl ester (48 % e.e.).

Extrinsic chiral porphyrins, where the porphyrin itself is not chiral but introduction of the chiral substituents makes them chiral, have been reported by Groves (ref. 24), Naruta (ref. 25), Mansuy (ref. 26), and Kodadek (ref. 27) and are applied to the enantioselective oxygenation of olefins.

4. Fluoro and Perfluoroalkylporphyrins

Introduction of fluoro or perfluoroalkyl substituents to porphyrin is expected to lead to two new features. (1) For perfluoroalkyl substituents, they affect the electronic properties of the porphyrin π -system. Particularly, the redox properties of the porphyrin ligand can be controlled by such strategy. Recently, there has been much interest in the unique redox properties of fluoroporphyrins to serve as catalysts and functional materials. (2) For both perfluoroalkyl and fluoro substituents, the ^{19}F nuclei serve as a probe, which sensitively reflects the local environment around the nuclei. The first porphyrin with fluorine was reported by LeGoff et al (ref. 28). We have developed the synthesis of porphyrin having trifluoromethyl groups at the pyrrole β -position.

Pyrrole having a trifluoromethyl group was prepared by the modified Knorr condensation reaction (ref. 29). Benzyl ester (**32**, $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$) instead of ethyl ester should be used as a protecting group in this route because the deprotection of the ethyl group by alkaline hydrolysis also hydrolyzes the trifluoromethyl group. The benzyl ester (**36**) was cleaved by hydrogenolysis to afford the pyrrolecarboxylic acid (**37**), which is then allowed to undergo the condensation-cyclization in the presence of $\text{Cu}(\text{OAc})_2$ template to afford the tetrakis(trifluoromethyl)porphyrin (**38**) (ref. 30). It should be noted that a pyrrole with two trifluoromethyl groups at the β -position did not undergo the cyclization-condensation reaction, owing to the very low reactivity toward electrophilic substitution at α -position of this pyrrole.

Another route to the trifluoroalkylpyrrole is to take advantage of the reaction of isonitrile (**40**). The reaction of β -fluoroalkyl- α,β -unsaturated ketone (**39**) with *p*-toluenesulfonylmethyl isocyanide (**40**) in the presence of NaH afforded the α,α -unsubstituted pyrrole (**41**, $\text{R} = \text{CF}_3$) in 44 % yield (ref. 31). Use of the hazardous HNO_2 can be avoided in this route. This pyrrole can be used as a precursor for porphyrin synthesis after formylation at the α -position via the Vilsmeier reaction.

The trifluoromethylporphyrins showed some interesting properties owing to the electron-withdrawing nature of the substituent. The iron(III) complex of **45** ($\text{R} = \text{CF}_3$) showed the reduction potential of -0.81 V , which should be compared with the value of -1.39 V for the corresponding non-

fluoroporphyrin (ref. 32). This property is utilized in the cytochrome P-450 type oxygenation catalyst, because the higher oxidation potential of fluoroporphyrin considerably inhibits the decomposition of the porphyrin catalyst during the oxygenation of olefins. Also, the electrophilic character of the high valence oxo-iron species becomes much improved compared to usual porphyrins. The iron complex of 5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)-2,3,7,8,12,13,17,18-octabromoporphyrin showed alkane hydroxylation (ref.

33).

The iron complex of the highly electron-deficient porphyrin having four trifluoromethyl groups at the pyrrole β -position (**45•Fe**) were used as a catalyst for aldol condensation of cyclohexanone (ref. 34). The catalytic activity and turnover numbers are high owing to the electron-deficient nature of the porphyrin.

Another important application of fluoroporphyrin is to use fluorine as a ^{19}F NMR probe. ^{19}F nucleus is detected with

high sensitivity and its observation is not interfered by the other resonances even in the complex between porphyrin and protein. The paramagnetic ^{19}F NMR of the myoglobin reconstituted with **46** was proved to be useful to probe the heme environment (ref. 35).

Ring-fluorinated porphyrins (47) are also reported (ref. 36). In the absorption spectrum of monofluoroporphyrin, almost no shift is observed while the Soret band of trifluoromethylporphyrin shows 10 nm red shift compared to the unsubstituted porphyrin. Therefore, the substituent effects of fluorine to the π -electron system of porphyrin are small. The ring-fluorinated porphyrin can be used as a mimic of prothetic heme and a useful NMR probe in the reconstitution studies of various heme proteins

5. Conclusion

Functionalization of porphyrin was achieved by the aid of synthetic organic chemistry. The rigid porphyrin framework and the design to inhibit the atropisomerization prevent the "quenching" of the active recognition groups since these are sequestered. Combinations of meso-substituents, β -substituents, and metals lead to a diverse range of functional hosts, which is able to recognize various guests, to undergo induced-fit complexation, or to have unique properties such as fluoroporphyrins. A number of spectroscopic methods such as ^1H NMR, ^{19}F NMR, UV-vis, and circular dichroism spectroscopy have been successfully used to probe the porphyrin-guest and porphyrin-protein interactions.

References and Notes

- (1) (a) Ogoshi, H.; Sugimoto, H.; Yoshida, Z. *Tetrahedron Lett.* **1976**, 4477. (b) Ogoshi, H.; Sugimoto, H.; Yoshida, Z. *Tetrahedron Lett.* **1976**, 4481. (c) Ogoshi, H.; Sugimoto, H.; Yoshida, Z. *Tetrahedron Lett.* **1977**, 169. (d) Ogoshi, H.; Sugimoto, H.; Yoshida, Z. *Tetrahedron Lett.* **1977**, 1515.
- (2) Battersby, A. R.; Buckley, D. G.; Hartley, S. G.; Turnbull, M. J. *Chem. Soc., Chem. Commun.* **1976**, 879.
- (3) Ogoshi, H.; Sugimoto, H.; Nishiguchi, T.; Watanabe, T.; Matsuda, Y.; Yoshida, Z. *Chem. Lett.* **1978**, 29.
- (4) (a) Aoyama, Y.; Yamagishi, A.; Asagawa, M.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1988**, *110*, 4076. (b) Aoyama, Y.; Asakawa, M.; Yamagishi, A.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1990**, *112*, 3145.
- (5) Mizutani, T.; Ema, T.; Yoshida, T.; Kuroda, Y.; Ogoshi, H. *Inorg. Chem.* **1993**, *32*, 2072.
- (6) Mizutani, T.; Ema, T.; Yoshida, T.; Renne, T.; Ogoshi, H. *Inorg. Chem.* **1994**, *33*, 3558.
- (7) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1991**, *113*, 6233.
- (8) Mizutani, T.; Murakami, T.; Kurahashi, T.; Ogoshi, H. *J. Org. Chem.* **1996**, *61*, 539.
- (9) Mizutani, T.; Murakami, T.; Matsumi, N.; Kurahashi, T.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1257.
- (10) Mizutani, T.; Murakami, T.; Ogoshi, H. *Tetrahedron Lett.* **1996**, in press.
- (11) Hayashi, T.; Miyahara, T.; Hashizume, N.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 2049.
- (12) Hayashi, T.; Asai, T.; Hokazono, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 12210.
- (13) Kuroda, Y.; Kawashima, A.; Urai, T.; Ogoshi, H. *Tetrahedron Lett.* **1995**, *36*, 8449.
- (14) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898.
- (15) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054.
- (16) Ogoshi, H.; Saita, K.; Sakurai, K.; Watanabe, T.; Toi, H.; Aoyama, Y. *Tetrahedron Lett.* **1986**, *27*, 6365.
- (17) (a) Mizutani, T.; Ema, T.; Tomita, T.; Kuroda, Y.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1993**, 520. (b) Mizutani, T.; Ema, T.; Tomita, T.; Kuroda, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1994**, *116*, 4240.
- (18) (a) Kuroda, Y.; Kato, Y.; Higashioji, T.; Ogoshi, H. *Angew. Chem.* **1993**, *105*, 774. (b) Kuroda, Y.; Kato, Y.; Higashioji, T.; Hasegawa, J.-y.; Kawanami, S.; Takahashi, M.; Shiraishi, N.; Tanabe, K.; Ogoshi, H. *J. Am. Chem. Soc.* **1995**, *117*, 10950.
- (19) Aoyama, Y.; Saita, K.; Toi, H.; Ogoshi, H.; Okamoto, Y. *Tetrahedron Lett.* **1987**, *28*, 4853.

- (20) Aoyama, Y.; Uzawa, T.; Saita, K.; Tanaka, Y.; Toi, H.; Ogoshi, H.; Okamoto, Y. *Tetrahedron Lett.* **1988**, 29, 5271.
- (21) Konishi, K.; Takahata, Y.; Aida, T.; Inoue, S.; Kuroda, R. *J. Am. Chem. Soc.* **1993**, 115, 1169.
- (22) Konishi, K.; Oda, K.-i.; Nishida, K.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1992**, 114, 1313.
- (23) (a) Crossley, M. J.; Hambley, T. W.; Mackay, L. G.; Try, A. C.; Walton, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1077. (b) Crossley, M. J.; Mackay, L. G.; Try, A. C. *J. Chem. Soc., Chem. Commun.* **1995**, 1925.
- (24) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, 105, 5791.
- (25) Naruta, Y.; Tani, F.; Ishihara, N.; Maruyama, K. *J. Am. Chem. Soc.* **1991**, 113, 6865.
- (26) Mansuy, D.; Battioni, P.; Renaud, J. P.; Guerin, P. *J. Chem. Soc., Chem. Commun.* **1985**, 155.
- (27) Maxwell, J. L.; O'Malley, S.; Brown, K. C.; Kodadek, T. *Organometallics* **1992**, 11, 645.
- (28) Kaesler, R. W.; LeGoff, E. *J. Org. Chem.* **1982**, 47, 5243.
- (29) Ogoshi, H.; Homma, M.; Yokota, K.; Toi, H.; Aoyama, Y. *Tetrahedron Lett.* **1983**, 24, 929.
- (30) Homma, M.; Aoyagi, K.; Aoyama, Y.; Ogoshi, H. *Tetrahedron Lett.* **1983**, 24, 4343.
- (31) Aoyagi, K.; Toi, H.; Aoyama, Y.; Ogoshi, H. *Chem. Lett.* **1988**, 1891.
- (32) Yoshimura, T.; Toi, H.; Inaba, S.; Ogoshi, H. *Inorg. Chem.* **1991**, 30, 4315.
- (33) Ellis, P. E.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, 105, 181. (b) Grinstaff, M. W.; Hill, M. G.; Labinger, J. A.; Gray, H. B. *Science* **1994**, 264, 1311.
- (34) Kuroda, Y.; Suzuki, Y.; Ogoshi, H. *Tetrahedron Lett.* **1994**, 35, 749.
- (35) Toi, H.; Homma, M.; Suzuki, A.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1791.
- (36) (a) Onda, H.; Toi, H.; Aoyama, Y.; Ogoshi, H. *Tetrahedron Lett.* **1985**, 26, 4221. (b) Suzuki, A.; Toi, H.; Aoyama, Y.; Ogoshi, H. *Heterocycles* **1992**, 33, 87.

(Received June 17, 1996)