tioenriched amines. Our results are comparable or superior to those reported using other metal catalysts.[3]

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Supplementary Material Available: Detailed experimental procedures for the asymmetric imine hydrogenations, as well as for the preparation and spectroscopic characterization of complex **1**, and the starting materials and products listed in Table I (14 pages). Ordering information is given on any current masthead page.

Direct Hydroxylation at the Meso Position of Gold(III) Tetraphenylporphyrin by Nucleophilic Addition: Novel Hydroxyphlorin Derivatives

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We report the first example of the direct nucleophilic addition of OH^- ion on a nonoxidized porphyrin ring, which affords a meso-saturated adduct having the same electronic structure as phlorin.

Porphyrin derivatives containing saturated meso carbon(s) are important intermediates not only in the biosynthesis[1] and the metabolism[2] of natural porphyrins but also in the redox chemistry and the synthesis[3] of various artificial porphyrins. "Phlorin"[4] and "isoporphyrin",[5] which have one saturated meso carbon, are two typical types of such derivatives and are clearly classified into group I and II as shown in Figure 1.[6] In redox reactions of the porphyrins, the phlorin and the isoporphyrin are formed through a π-dianion (Figure 1a) and a π-dication (Figure 1b), respectively. On the other hand, similar derivatives can be obtained by alternative synthetic procedures without the redox process. For instance, meso-saturated porphyrin derivatives classified into group II have been directly synthesized by electrophilic addition to the porphyrin ring (Figure 1d).[7] In this case, the electrophilic adducts obtained have the same electronic structure as the isoporphyrin. However, direct nucleophilic addition to the nonoxidized porphyrin ring has not been reported except for reduction with BH_4^-.[8] The lack of nucleophilic addition is ascribed to the poor electrophilicity of the conventional metalloporphyrins used so far. With this in mind, direct nucleophilic addition is accomplished by use of gold(III) porphyrins, which are strong electrophiles. The obtained products are novel nucleophilic adducts, namely, "hydroxyphlorin", classified into group I.

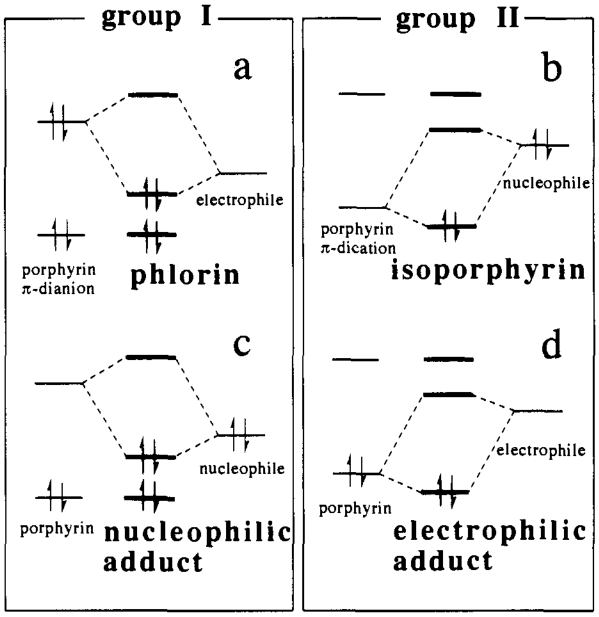


Figure 1. Schematic representation of orbital interactions of porphyrins with nucleophile or electrophile.

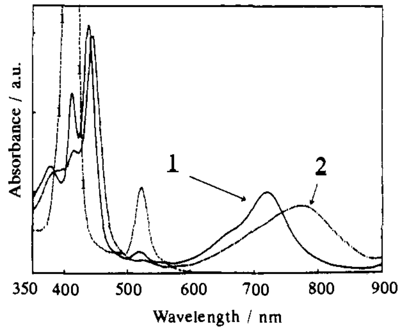
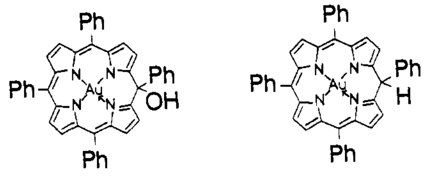


Figure 2. Absorption spectra of $[\mathrm{Au^{III}(TPP)}]^+\mathrm{Cl^-}$ (- - -), nucleophilic adduct $[\mathrm{Au^{III}(TPP\text{-}OH)}]$ (**1**) (—), and phlorin $[\mathrm{Au^{III}(TPP\text{-}H)}]$ (**2**) (- • - • -) in DMSO.

Chart I



1 2

Tetra-*n*-butylammonium hydroxide (TBAOH) 10% methanol solution or NaOH aqueous solution was used as a source of OH^- ion. Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were used as solvents. Gold(III) porphyrins ($[\mathrm{Au^{III}(TPP)}]^+\mathrm{Cl^-}$, $[\mathrm{Au^{III}(TSPP)}]^+\mathrm{Cl^-}$, $[\mathrm{Au^{III}(TCPP)}]^+\mathrm{Cl^-}$, and $[\mathrm{Au^{III}(TPyP)}]^+\mathrm{Cl^-}$) and the other metalloporphyrins ($\mathrm{Pd^{II}(TPP)}$, $\mathrm{Cu^{II}(TPP)}$, $\mathrm{Cd^{II}(TPP)}$, and $[\mathrm{Mn^{III}(TPP)}]^+\mathrm{Cl^-}$) were synthesized and purified by the reported procedures.[9,10]

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(6) The phlorin formed through an electrophilic attack at a meso carbon of a porphyrin dianion (Figure 1a) has two more electrons in the porphyrin moiety than the isoporphyrin formed through a nucleophilic attack at a meso carbon of a porphyrin dication (Figure 1b).

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(10) TPP, *meso*-tetraphenylporphyrin; TSPP, *meso*-tetrakis(4-sulfonatophenyl)porphyrin; TCPP, *meso*-tetrakis(4-carboxyphenyl)porphyrin; TPyP, *meso*-tetrakis(4-pyridyl)porphyrin.

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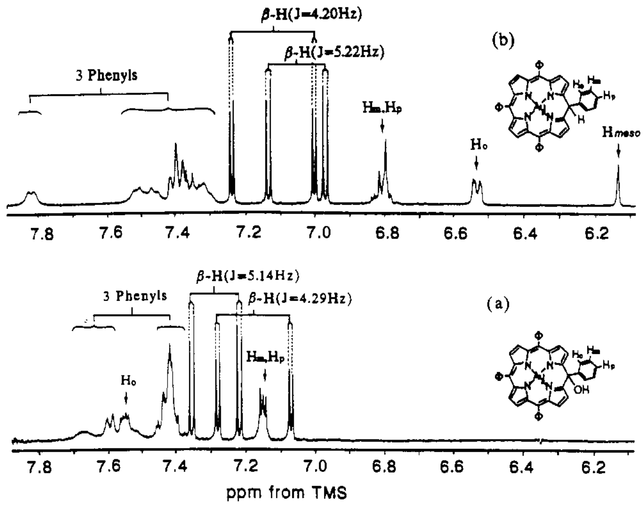

Figure 3. The 400-MHz ^{1}H NMR spectra of (a) [Au^{III}(TPP-OH)] (**1**) and (b) [Au^{III}(TPP-H)] (**2**) in cyclohexane-d_{12}.

The nucleophilic addition of OH^- to gold(III) tetraphenylporphine chloride[11] ([Au^{III}(TPP)]$^+$Cl$^-$) was performed by the following procedure. A slight excess of aqueous NaOH was added to a DMSO solution of [Au^{III}(TPP)]$^+$Cl$^-$ at room temperature. As NaOH was added, the solution color changed form red to greenish brown. This reaction proceeded in other solvents such as DMF and with other OH^- ion sources such as TBAOH. The greenish brown product **1** (Chart I) was isolated by extraction with *n*-hexane. The *n*-hexane solution was washed twice with water to remove ionic species and evaporated to remove the solvent, and then the product **1** was dried in vacuo at room temperature. The absorption spectrum of **1** (Figure 2) differs clearly from that of π-radical species, metal redox species, ligand exchange species, and isoporphyrins.[7,9] It is noteworthy that the absorption spectrum of **1** resembles that of gold(III) tetraphenylphlorin **2** in the features of the visible and the near-infrared absorption bands (Figure 2) except for the blue shifts of the absorption maxima.[12] These results suggest that the π-electron system of the porphyrin ring of **1** is broken as is that of **2**. The following data were obtained for the molecular structure of **1**. (i) The molecular weight (MW) of **1** determined by secondary ion mass spectrometry (SIMS) was 826, indicating that **1** was a monohydroxylated product of [Au^{III}(TPP)]$^+$ (MW = 809).[13] (ii) The MH$^+$ SIMS peak indicates that the product is a neutral species.[13] (iii) Bands at 3572 and 3607 cm^{-1} in the infrared absorption spectrum of **1** in CCl_4 revealed that the OH group was attached as an alcoholic OH (supplementary material). (iv) Although [Au^{III}(TPP)]$^+$Cl$^-$ exhibits weak infrared absorption in the range 1400–1700 cm^{-1}, **1** has very strong bands in this region as does **2** (supplementary material). These bands arise from the activation of a porphyrin vibration by the breaking of D_{4h} symmetry.[14] (v) As shown in Figure 3, the ^{1}H NMR spectrum for the β-protons of **1** consists of two AB quartets, which indicates that **1** has C_2 symmetry due to addition at one meso carbon.[15] Consequently, it was concluded that **1** is gold (III) tetraphenylporphyrin monohydroxylated at the meso position, namely, "hydroxyphlorin" (Au^{III}(TPP-OH)).[16] The OH group of **1** was reversibly eliminated by the addition of acid, but the phenyl group was not eliminated. We could understand **1** as Meisenheimer complex analogous to the nucleophilic adduct derived from trinitrobenzene and hydroxide anion.

The optical spectra of isoporphyrins containing a divalent or trivalent central metal are quite different from the spectra of **1** and **2**.[7] The isoporphyrins have two strong absorption peaks in the near-IR region, but the phlorins have only one broad peak in the near-IR region. Therefore the isoporphyrin and the phlorin can be easily differentiated by the absorption spectra.

For other gold(III) porphyrins ([Au^{III}(TPyP)]$^+$Cl$^-$, [Au^{III}(TSPP)]$^+$Cl$^-$, and [Au^{III}(TCPP)]$^+$Cl$^-$), the corresponding nucleophilic adducts were obtained by the same procedure.[17] On the other hand, nucleophilic adducts of Pd^{II}(TPP), Cu^{II}(TPP), Cd^{II}(TPP), and [Mn^{III}(TPP)]$^+$Cl$^-$ were not formed even in the DMSO solution saturated with TBAOH. These results are interpreted in terms of differences in the electrophilicity of the porphyrin ring, which are induced by the central metal. From these results, we expect that similar nucleophilic addition occurs in other porphyrins with high-valence metals such as P(V). The present reaction is regarded as not only an important feature of porphyrins with high-valence metals but also a novel route for the modification of porphyrins.

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Supplementary Material Available: Infrared absorption spectra of **1**, **2**, and [Au^{III}(TPP)]$^+$Cl$^-$ (1 page). Ordering information is given on any current masthead page.

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(11) Anal. Calcd for [Au^{III}(TPP)]$^+$Cl$^-$·2H_2O, $C_{44}H_{32}N_4O_2AuCl$: C, 60.0; H, 3.54; N, 6.49; Cl, 4.04. Found: C, 60.5; H, 3.43; N, 6.35; Cl, 4.02.

(12) The absorption maxima of **1** in C_6H_{12} are 439 nm ($\epsilon = 6.9 \times 10^4$) and 726 nm ($\epsilon = 1.9 \times 10^4$). The absorption maxima of **2** in C_6H_{12} are 443 nm ($\epsilon = 5.8 \times 10^4$) and 756 nm ($\epsilon = 1.6 \times 10^4$). The phlorin **2** was obtained by the chemical reduction of [Au^{III}(TPP)]$^+$ according to ref 8.

(13) A Hitachi M80 was used for the secondary ion mass spectrometry. Obtained parent peaks are 827 (MH$^+$) for **1**, 811 (MH$^+$) for **2**, and 809 (M$^+$) for [Au^{III}(TPP)]$^+$.

(14) Bürger, H. *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 11.

(15) The two AB quartets in the ^{1}H NMR spectra of the β-protons were observed in both phlorin[4] and isoporphyrin.[5] The ^{1}H NMR spectral data of the β-protons of **1** are as follows: 7.07 (d, 2 H, J_{HH} = 4.29 Hz), 7.22 (d, 2 H, J_{HH} = 5.14 Hz), 7.28 (d, 2 H, J_{HH} = 4.29 Hz), 7.35 ppm (d, 2 H, J_{HH} = 5.14 Hz). Those of **2** are as follows: 6.97 (d, 2 H, J_{HH} = 5.22 Hz), 7.00 (d, 2 H, J_{HH} = 4.20 Hz), 7.14 (d, 2 H, J_{HH} = 5.22 Hz), 7.24 ppm (d, 2 H, J_{HH} = 4.20 Hz). The chemical shifts of **1** are at lower field than those of **2** because of the presence of an O atom in **1**.

(16) An IUPAC name for **1** is inconvenient for the distinction from the corresponding isoporphyrin. As a trivial name, the term "hydroxyphlorin" could be conveniently used for the designation of **1** in order to distinguish it from the normal phlorins and isoporphyrins.

(17) Absorption maxima of hydroxyphlorins in DMSO are as follows: 438 and 719 nm for [Au^{III}(TPyP-OH)], 441 and 725 nm for [Au^{III}(TSPP-OH)], and 441 and 727 nm for [Au^{III}(TCPP-OH)].

Role of F Centers in the Oxidative Coupling of Methane to Ethane over Li-Promoted MgO Catalysts

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We report a study of the partial oxidation of methane to ethane over a model MgO catalyst prepared under well-controlled, ultrahigh vacuum (UHV) conditions using a combination of surface science techniques and elevated pressure kinetic measurements. The results indicate that [Li$^+$O$^-$] centers are not likely to be directly involved in the methane activation step, but rather they promote the production of color centers in the near-surface region which are responsible for this key step in the methane coupling reaction.

Li-promoted MgO films were synthesized under UHV conditions by co-depositing Mg and Li onto a clean Mo(100) surface in a background pressure of oxygen. A detailed description regarding film synthesis and characterization will be given elsewhere.[1] The oxide films were pretreated by heating in oxygen

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