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(σ-Alkyl)iron Complexes as Intermediates in (Porphinato)iron-Mediated Reduction of Alkenes and Alkynes with Sodium Borohydride

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The (porphinato)irons promote the reduction of alkenes and alkynes with NaBH$_4$ in anaerobic benzene–ethanol. Styrene is reduced to 2,3-diphenylbutane and ethylbenzene, whose precursors have been assumed to be the (σ-alkyl)iron(III) and -iron(II) porphyrin complexes, respectively. The (σ-alkyl)iron(III) porphyrin complex has the reactivity of the alkyl radical while the (σ-alkyl)iron(II) porphyrin complex shows the nature of the carbanion.

Cytochrome P-450 catalyzes oxidation of organic compounds with dioxygen.[1] It has been elucidated that (porphinato)iron(III) is reduced to iron(II) via an electron transfer from NADPH and the dioxygen–(porphinato)-iron(II) complex further accepts an electron and two protons to form an iron(V) oxo porphyrin or iron(IV) oxo porphyrin cation radical.[2,3] In certain cases, however, such a dioxygen-activation process is inhibited by substrates, such as halogenated alkanes,[4] epoxides,[5] amine oxides,[6] and nitroarenes.[7] These substrates are converted to their reduced forms through the (porphinato)iron-catalyzed reduction by NADPH. The σ-alkyl iron porphyrin complexes have been postulated as the key intermediates in the reductive dehalogenation of haloalkanes.[4]

In order to clarify the mechanism of the cytochrome P-450-catalyzed monooxygenation, lots of model reactions have been examined so far.[3,8] As one of the models of the cytochrome P-450-catalyzed monooxygenation, the metalloporphyrin–BH$_4^-$–O$_2$ system has been applied by Tabushi and Koga.[9] They used NaBH$_4$–(TPP)Mn^{III}Cl (TPP: 5,-10,15,20-tetraphenylporphyrin dianion) for the monooxygenation of cyclohexene and assumed that cyclohexene oxide is an initial product which is reduced to cyclohexanol, a main product, with NaBH$_4$. Similar oxygenation using the Mn^{III}, Co^{II}, and Fe^{III} complexes of TPP and BH$_4^-$ has been studied.[10–12] Except for the (TPP)Co^{II} system,[11] the reaction mechanisms for the metalloporphyrin-catalyzed monooxygenation of alkenes have not been studied in detail. Recently, we have demonstrated that the (σ-alkyl)-iron porphyrin complex is an intermediate in the hydroxylation of styrene catalyzed by an iron complex of a cationic porphyrin in aerobic water containing NaBH$_4$.[13] Besides these biomimetic oxygenations, few studies in the model systems have been reported for the metalloporphyrin-catalyzed reduction of organic compounds. The rhodium(III) and iron(III) complexes of porphyrins catalyze the reduction of ketones and sulfoxides, respectively, with NaBH$_4$.[14,15] Similarly, nitrobenzene and *p*-chloronitrobenzene are reduced to anilines by NaBH$_4$ in diglyme in the presence of (TPP)Fe^{III}Cl.[16] In the previous communication,[17] we briefly reported the (porphinato)iron-catalyzed reduction of styrene with NaBH$_4$ in benzene–ethanol where the (σ-alkyl)iron(III) porphyrin complex is formed as a reaction intermediate. The present paper deals with the details in the (porphinato)iron-mediated reduction of unsaturated hydrocarbons with NaBH$_4$ and the mechanism involving the reactivities of the (σ-alkyl)iron(III) and -iron(II) porphyrin complexes.

Results

Reduction Products of Alkenes and Alkynes. Although both alkenes and alkynes do not react with NaBH$_4$ in organic solvents without any other additive, these unsaturated compounds (1.5 mmol) are reduced by NaBH$_4$ (200 mol %; mol % toward the substrate) in N$_2$-saturated benzene–ethanol (1:1) containing 10 mol % (TPP)Fe^{III}Cl or (ClTPP)Fe^{III}Cl (ClTPP: 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrin dianion). Table I shows the reduction products of alkenes and alkynes. In the reaction of styrene (entries 1 and 2), ethylbenzene and *meso*- and (±)-2,3-diphenylbutanes are formed. 2,3-Diphenylbutane should be the coupling product of the 1-phenylethyl radicals (vide

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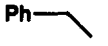
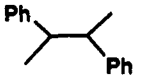
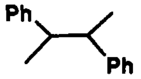
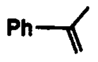
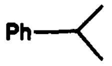
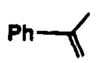
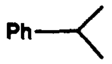
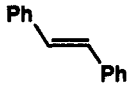
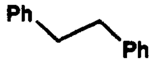
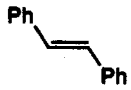
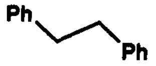
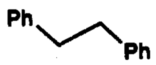
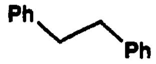
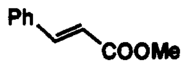
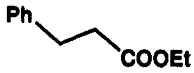
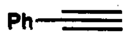
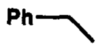
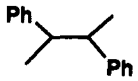
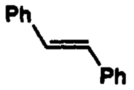
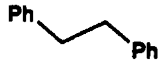
Table I. (Porphinato)iron-Mediated Reduction of Alkenes and Alkynes with $NaBH_4$ in Benzene–Ethanol (1:1) at Room Temperature

entry	substrate	catalyst	reaction time/h	product	yield/%[a]
1		(TPP)Fe^{III}Cl	6		13 (13)
					36 (36)
2		(ClTPP)Fe^{III}Cl	6		76 (76)
					13 (13)
3		(TPP)Fe^{III}Cl	6		13 (13)
					75 (75)
4		(ClTPP)Fe^{III}Cl	1		10 (10)
					74 (74)
5		(TPP)Fe^{III}Cl	24		17 (29)
6		(ClTPP)Fe^{III}Cl	24		27 (67)
7		(TPP)Fe^{III}Cl	24		14 (26)
8		(ClTPP)Fe^{III}Cl	24		18 (41)
9		(TPP)Fe^{III}Cl	24		70 (70)
10		(TPP)Fe^{III}Cl	24		17 (17)
					23 (23)
11		(TPP)Fe^{III}Cl	1		77 (77)
					12 (12)
					1 (1)

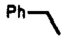
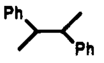
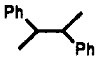
[a] Yields based on an initial concentration of the substrates. The values in parentheses are the yields based on the consumed substrates.

infra). The formation of the coupling product becomes more remarkable in the reactions of α-methylstyrene (entries 3 and 4). Both *cis*- and *trans*-stilbenes are less reactive compared with the styrenes, and 1,2-diphenylethane is the only product which can be detected (entries 5–8). Interestingly, methyl cinnamate is reduced and transesterified to afford ethyl 3-phenylpropionate (entry 9). Alkynes such as phenylacetylene and 1,2-diphenylacetylene are also reduced (entries 10 and 11).

Solvent Effects. Table II summarizes the results of the solvent effects on the (porphinato)iron-mediated reduction of styrene with $NaBH_4$. The proton-donating ability of the solvent is essential for forming ethylbenzene. In ethanol (entries 1 and 7), styrene is consumed very rapidly and ethylbenzene is obtained in relatively good yield compared with those in the mixed solvents such as benzene–ethanol (entries 2 and 8) and acetonitrile–ethanol (entry 4). In contrast with the reactions in the protic solvents, the formation of ethylbenzene could not be detected in the reactions in the aprotic solvents such as benzene (entries 5 and 11) and benzene–acetonitrile (entry 6). 2,3-Diphenylbutane is the sole product which is detected by means of GLC. In aprotic solvents, over 80% of the consumed styrene is converted to the unknown product(s). Polystyrene may be generated in aprotic solvents. These results strongly suggest that ethylbenzene is formed by the proton transfer from solvent to 1-phenylethanide ($[C_6H_5CHCH_3]^-$) or its complex with (porphinato)iron.

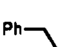
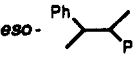
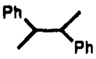
Effects of Free-Radical Trap. TEMPO (2,2,6,6-

Table II. Solvent Effects on (Porphinato)iron-Mediated Reduction of Styrene with $NaBH_4$ at Room Temperature

				yield/%		
entry	catalyst	solvent[a]	reaction time[b]/h		meso- 	(±)- 
1	(TPP)Fe^{III}Cl	C_2H_5OH	1	65	6	8
2	(TPP)Fe^{III}Cl	$C_6H_6C_2H_5OH$	6	13	17	19
3	(TPP)Fe^{III}Cl[c]	$C_6H_6C_2H_5OH$	6	10	6	4
4	(TPP)Fe^{III}Cl	$CH_3CNC_2H_5OH$	4	38	13	12
5	(TPP)Fe^{III}Cl[d]	C_6H_6	24	0	7	7
6	(TPP)Fe^{III}Cl[d]	$C_6H_6CH_3CN$	24	0	10	10
7	(ClTPP)Fe^{III}Cl	C_2H_5OH	1	81	5	6
8	(ClTPP)Fe^{III}Cl	$C_6H_6C_2H_5OH$	6	76	6	7
9	(ClTPP)Fe^{III}Cl[c]	$C_6H_6C_2H_5OH$	6	60	1	1
10	(ClTPP)Fe^{III}Cl	$C_6H_6(CH_3)_2CHOH$	24	4	12	11
11	(ClTPP)Fe^{III}Cl[d]	C_6H_6	24	0	6	6

[a] The ratio of the mixed solvents is 1:1 (v/v). [b] Times for complete consumption of styrene. [c] In these systems, the reactions were carried out in the presence of TEMPO (100 mol %). [d] In these systems, 15-crown-5 was used to dissolve $NaBH_4$.

Table III. (TPP)Fe-Mediated Reduction of Styreme with $NaBH_4$ in Strictly Degassed Benzene–Ethanol (1:1) at Room Temperature[a]

		yield[b]/%		
entry	reaction time/h		meso- 	(±)- 
1	6	25 (32)	5 (6)	5 (6)
2	24	65 (66)	5 (5)	5 (5)
3	24	22 (22)	17 (17)	18 (18)

[a] The reaction conditions are described in the caption of Figure 1. In entries 1 and 2, the reactions were carried out in the completely degassed solvent. In entry 3, the reaction was carried out in the N_2-saturated solvent. [b] Yields based on initial concentration of styrene. The values in parentheses are the yields based on consumed styrene.

tetramethylpyridinyloxy) has been used as a free-radical trap.[18] The effects of TEMPO were studied for the (porphinato)iron-mediated reduction of styrene with $NaBH_4$ in benzene–ethanol (entries 3 and 9 in Table II). Addition of TEMPO (100 mol % toward styrene) causes significant reduction in the yield of 2,3-diphenylbutane, while the formation of ethylbenzene is slightly affected by this free-radical trap. It can be concluded, therefore, that 2,3-diphenylbutane is formed via a coupling reaction of the 1-phenylethyl radicals.

Effects of Oxygen. A convenient procedure to prepare the anaerobic conditions is described in the Experimental Section. The air in the reaction vessel was evacuated by a water pump, and the vessel was filled with the nitrogen gas. However, the oxygen could not be removed completely by such an easy procedure. In order to check the effects of oxygen remaining in the reaction system, we tried to degas the reaction tube by the freeze–pump–thaw cycles (five times). The results obtained under the strictly anaerobic conditions are shown in Table III. The yield of 2,3-diphenylbutane does not exceed 10% under such conditions. This result is very suggestive for elucidating the mechanism of the 2,3-diphenylbutane formation. The time course of the reaction is shown in Figure 1. The conversion of styrene and the yields of the reduction products at each reaction time were obtained from each sample prepared independently. At the initial stage of the reaction, 2,3-diphenylbutane is formed more rapidly than ethylbenzene and the formation of this radical-coupling product is saturated at 10% after 3 h. Meanwhile, the formation of ethylbenzene becomes remarkable after the formation of 2,3-diphenylbutane stops. In the present experiments, the reduction was carried out using 10 mol % (TPP)Fe^{III}Cl. The yield of 2,3-diphenylbutane well corresponds to the mol % of (TPP)Fe^{III}Cl toward styrene, suggesting that this product is formed by an action of the iron(III) complex of the porphyrin whose valency is altered to iron(II) upon formation of 2,3-diphenylbutane and that (TPP)Fe^{II} is inactive toward the 2,3-diphenylbutane production. The induction period for generation of ethylbenzene clearly indicates that the new iron complex of the porphyrin, (TPP)Fe^{II}, catalyzes the formation of ethylbenzene.

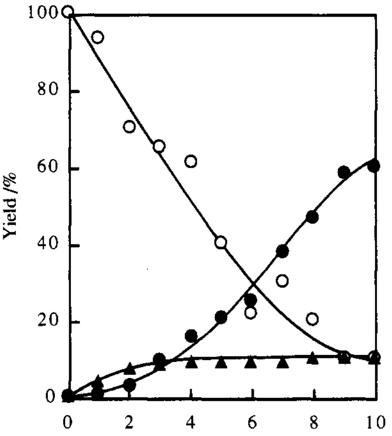


Figure 1. Progress in the disappearance of styrene (○) and in the formation of 2,3-diphenylbutane (▲) and ethylbenzene (●) in the reaction of styrene (0.15 mmol) with $NaBH_4$ (0.3 mmol) in strictly degassed benzene–ethanol (1:1, 0.8 mL) containing (TPP)Fe^{III}Cl (0.015 mmol) at room temperature.

Absorption Spectroscopy. The absorption spectral changes at the visible region were followed after $NaBH_4$ (100 mol %) was added into the mixture of styrene (0.18 mol dm^{-3}) and (TPP)Fe^{III}Cl (1.8×10^{-5} mol dm^{-3}, 0.01 mol %) in benzene–ethanol (1:1 under the strictly degassed conditions (Figure 2). After addition of $NaBH_4$, the absorption spectrum of (TPP)Fe^{III}Cl immediately changes to the new one having λ_{max} at 418, 580, and 635 nm (sh). The same absorption spectrum was obtained even in the absence of styrene, and this new spectrum is in good agreement with the spectrum of (porphinato)iron(III) ethoxide, (TPP)Fe^{III}OC$_2$H$_5$, prepared by the method described in the literature.[19] Within 5 min, the absorption spectrum changes again only in the case where styrene exists and the final spectrum having λ_{max} at 428, 540, 553

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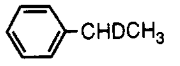
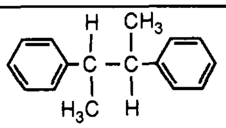
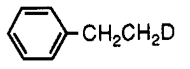
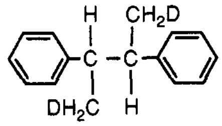
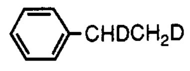
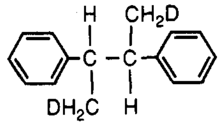
(18) For example: Daikh, B. E.; Finke, R. G. *J. Am. Chem. Soc.* 1992, *114*, 2938.

Table IV. Deuterium Incorporation in the (ClTPP)Fe-Mediated Reduction of Styrene at Room Temperature

system	products	
$NaBH_4/C_6H_6C_2H_5OD$		
$NaBD_4/C_6H_6C_2H_5OH$		
$NaBD_4/C_6H_6C_2H_5OD$		

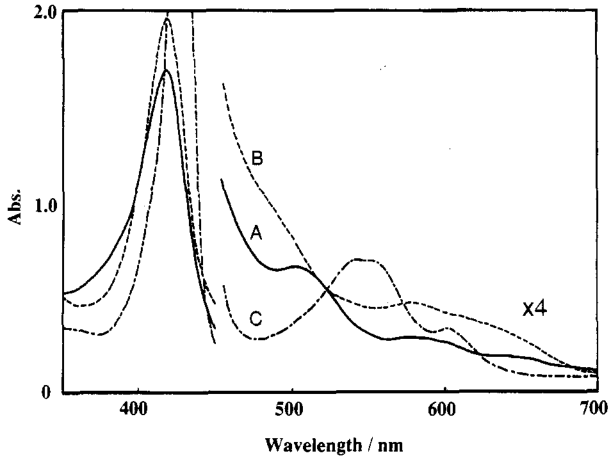


Figure 2. Absorption spectral changes of $(TPP)Fe^{III}Cl$ (1.8×10^{-5} mol dm^{-3}) in strictly degassed benzene–ethanol (1:1) after mixing with $NaBH_4$ (0.18 mol dm^{-3}) and styrene (0.18 mol dm^{-3}) at room temperature. Line A is the absorption spectrum of $(TPP)Fe^{III}Cl$ in benzene–ethanol which immediately changes to line B due to $(TPP)Fe^{III}OC_2H_5$ upon mixing with $NaBH_4$ and styrene. Within 5 min after mixing, the spectrum changes again to line C which is ascribed to $(TPP)Fe^{II}(HOC_2H_5)_2$.

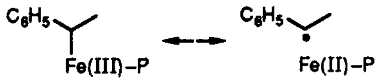
(sh), and 602 nm seems to be due to $(TPP)Fe^{II}(C_2H_5OH)_2$.[20]

Deuterium Incorporation. In order to clarify the origins of the hydrogens in the reduction products, the deuterium incorporation was studied by using $NaBD_4$ and C_2H_5OD. The reactions were carried out in N_2-saturated benzene–ethanol (1:1). The products were analyzed by means of GC–MS and ^1H NMR spectroscopies. The results are shown in Table IV, which strongly suggests that a hydrogen of each methyl group of ethylbenzene and 2,3-diphenylbutane is donated from $NaBH_4$ as a hydride and a hydrogen of the α-position of ethylbenzene comes from the protic solvent as a proton.

Discussion

The alkenes and the alkynes such as styrene, α-methylstyrene, *trans*- and *cis*-stilbenes, methyl cinnamate, phenylacetylene, and 1,2-diphenylacetylene are reduced with $NaBH_4$ in organic solvents by the action of the (porphinato)iron complexes. To the best of our knowledge, this is the first case of the (porphinato)iron-mediated reduction of unsaturated hydrocarbons with BH_4^-. In the present study, the reduction of styrene has been applied as a mechanistic probe.

In the reaction of styrene, 2,3-diphenylbutane and ethylbenzene are the products. Although $(TPP)Fe^{III}Cl$ and $(ClTPP)Fe^{III}Cl$ mediate the formation of 2,3-diphenylbutane, this reaction is not catalyzed by these porphyrin complexes in the system where oxygen is completely removed. The fact that the final yield of this radical-coupling product corresponds to the mol % of $(TPP)Fe^{III}Cl$ toward styrene strongly suggests that the precursor of 2,3-diphenylbutane is the (σ-alkyl)iron(III) porphyrin complex, $(TPP)Fe^{III}CH(CH_3)(C_6H_5)$. This ($\sigma$-alkyl)iron(III) porphyrin complex should have the nature of the $(TPP)Fe^{II}$–1-phenylethyl radical, $[(TPP)Fe^{II}][{}^{\bullet}CH(CH_3)(C_6H_5)]$:



(1)

A bimolecular reaction of $(TPP)Fe^{III}CH(CH_3)(C_6H_5)$ itself seems to afford 2,3-diphenylbutane and (porphinato)iron(II). It is very hard to consider that the 1-phenylethyl radicals released from the (porphinato)iron couple react with each other in solution, because 2-propanol, a good hydrogen donor, does not inhibit the formation of 2,3-diphenylbutane (Table II, entry 10). The coupling to afford 2,3-diphenylbutane and $(TPP)Fe^{II}$ may occur when the (σ-1-phenylethyl)iron(III) porphyrin molecules collide with each other. The formation of $(TPP)Fe^{III}CH(CH_3)(C_6H_5)$ could not be detected by means of electronic absorption and ^1H NMR spectroscopies. We have postulated the same (σ-alkyl)iron porphyrin complex as an intermediate for the (porphinato)iron-catalyzed addition reaction of thiophenol (origin of the thiol is diphenyl disulfide) to styrene.[21] We have also assumed a similar intermediate for the hydroxylation of styrene catalyzed by the iron complex of the cationic porphyrin in water containing $NaBH_4$.[13] In all of our studies, the (σ-1-phenylethyl)iron(III) porphyrins have not been detected by means of electronic absorption and/or ^1H NMR spectroscopy. Recently, Setsune et al. measured the ^1H NMR spectra of (σ-alkyl)iron(III) TPP complexes prepared by the $NaBH_4$ reduction of 1- and 2-hexenes and 1-, 2-, and 3-pentenes in toluene–methanol containing

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$(TPP)Fe^{III}Cl$.[22] These (σ-alkyl)iron(III) complexes isolated by Setsune et al. should be more stable than (σ-1-phenylethyl)iron(III) TPP because of their poor reactivity in the coupling reactions. It has been known that the secondary and tertiary alkyliron(III) porphyrin complexes are very unstable because of the occurrence of radical reactions.[23] Indeed, the coupling product, 2,3-dimethyl-2,3-diphenylbutane, is obtained in good yield in N_2-saturated benzene–ethanol when α-methylstyrene is used as a substrate (entries 3 and 4 in Table I). In the case of α-methylstyrene, the tertiary alkyliron(III) porphyrin complexes are expected to be formed as the intermediates.

$(TPP)Fe^{III}Cl$ in benzene–ethanol is initially converted to (porphinato)iron(III) ethoxide, $(TPP)Fe^{III}OC_2H_5$, through the reaction with $NaBH_4$. $(TPP)Fe^{III}OC_2H_5$ is detected by means of visible absorption spectroscopy (see Figure 2). On the basis of the fact that the hydrogen evolution was remarkable at the initial stage of the reaction, the following scheme may be considered for the 2,3-diphenylbutane formation:

$$(TPP)Fe^{III}Cl + NaBH_4 + C_2H_5OH \rightarrow (TPP)Fe^{III}OC_2H_5 + BH_3 + NaCl + H_2 \tag{2}$$

$$(TPP)Fe^{III}OC_2H_5 + C_6H_5CH{=}CH_2 + BH_3 \rightarrow (TPP)Fe^{III}CH(CH_3)(C_6H_5) + BH_2(OC_2H_5) \tag{3}$$

$$2(TPP)Fe^{III}CH(CH_3)(C_6H_5) \rightarrow (C_6H_5)(CH_3)CHCH(CH_3)(C_6H_5) + 2(TPP)Fe^{II} \tag{4}$$

$$(TPP)Fe^{II} + 2C_2H_5OH \rightleftharpoons (TPP)Fe^{II}(C_2H_5OH)_2 \tag{5}$$

$$BH_2(OC_2H_5) + C_2H_5OH \rightleftharpoons (C_2H_5OH)BH_2(OC_2H_5) \tag{6}$$

Since (porphinato)iron(II) cannot be oxidized to the original iron(III) complex in the absence of oxygen, the formation of 2,3-diphenylbutane stops when $(TPP)Fe^{III}Cl$ is converted completely to $(TPP)Fe^{II}(C_2H_5OH)_2$. The induction period exists in the formation of ethylbenzene (see Figure 1), clearly indicating that ethylbenzene is prepared by the action of the (porphinato)iron(II) complex. The results of the deuterium incorporation reveal that the precursor of ethylbenzene is 1-phenylethanide ($[C_6H_5CHCH_3]^-$) which accepts a proton from the protic solvent, ethanol, to afford ethylbenzene. It is quite reasonable to consider, therefore, that the (σ-1-phenylethyl)iron(II) TPP anion complex is formed as an intermediate in the ethylbenzene formation:

$$\begin{aligned}&(TPP)Fe^{II} + C_6H_5CH{=}CH_2 + (C_2H_5OH)BH_2(OC_2H_5) \rightarrow [(TPP)Fe^{II}CH(CH_3)(C_6H_5)]^- + \\ &(C_2H_5OH)BH(OC_2H_5) \rightarrow (TPP)Fe^{II} + C_6H_5CH_2CH_3 + BH(OC_2H_5)_2\end{aligned} \tag{7}$$

The catalysis of the (porphinato)iron(II) complex in the reduction of styrene to ethylbenzene can be well interpreted in terms of eq 7. The low reactivity of *cis*- and *trans*-stilbenes toward the reduction with $NaBH_4$ can also be explained by the fact that the steric hindrance due to the phenyl groups inhibits the formation of the (σ-alkyl)iron porphyrin complexes. Balch et al.[24] have found that the diamagnetic (σ-ethyl)iron(II) TPP complex can be prepared from the reaction of the paramagnetic (σ-ethyl)iron(III) TPP complex with lithium triethylborohydride ($LiHB(C_2H_5)_3$, Super-Hydride) in aprotic solvent and that $(TPP)Fe^{II}C_2H_5$ is easily oxidized by oxygen to give $(TPP)Fe^{III}C_2H_5$ while it is very stable in the absence of oxygen. In the experiments where oxygen is removed by a convenient procedure, $(TPP)Fe^{II}$ is oxidized to $(TPP)Fe^{III}$ by remaining oxygen, resulting in the catalysis of (porphinato)iron(III) for the 2,3-diphenylbutane formation.

The alkynes seems to be initially reduced to the corresponding alkenes by $NaBH_4$. Although the mechanism for the (porphinato)iron-catalyzed reduction of alkyne to alkene with $NaBH_4$ has not been studied in detail, the (σ-alkenyl)iron porphyrin complexes[25] may be generated intermediately. The transesterification in the reaction of methyl cinnamate may take place with a nucleophilic attack of $(TPP)Fe^{III}OC_2H_5$ to the methyl cinnamate and/or methyl 3-phenylpropionate. The studies on the mechanisms for these reactions are now in progress.

Experimental Section

Chemicals. $(TPP)Fe^{III}Cl$ and $(ClTPP)Fe^{III}Cl$ were prepared and purified according to the procedures described in the literatures.[26,27] All alkenes and alkynes (reagent grade) were purchased (Nacalai) and used without further purification. $NaBH_4$ (Nacalai), $NaBD_4$ (Aldrich), and C_2H_5OD (CEA) were commercially obtained. Organic solvents were dried by appropriate methods and distilled prior to use. 2,3-Diphenylbutane was prepared according to the procedure shown in the literature[28] and meso and (±) isomers were isolated by silica gel column chromatography with hexane. *meso*-2,3-Diphenylbutane was recrystallized from methanol.

Measurements. The visible absorption spectra were taken on a Shimadzu UV200S spectrophotometer. The 400-MHz ^1H NMR spectra were measured with a JEOL JNM-GX400 spectrometer at 23 ± 0.5 °C. The GC–MS spectra were recorded on a Hitachi M-80B or a Shimadzu QP2000 spectrometer. For GLC analysis, a Shimadzu GC-8A gas chromatograph having a Thermon 1000 glass column (1 m) was used.

General Procedures of Reduction. A typical example of the (porphinato)iron-mediated reduction of unsaturated hydrocarbons is shown below. The mixture of $(TPP)Fe^{III}Cl$ (108 mg, 0.15 mmol), $NaBH_4$ (115 mg, 3.0 mmol), and biphenyl (25 mg, an internal standard for GLC) was placed in a 30-mL two-necked flask. The flask was sealed by a silicone cap and a three-way glass cock with a rubber balloon filled with the nitrogen gas. The reaction vessel was evacuated by a water pump and then filled with the nitrogen gas in the balloon. After the four-time evacuation–charging with N_2 cycles, styrene (160 mg, 1.5 mmol) in N_2-saturated benzene–ethanol (8 mL) was injected into the

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vessel using a syringe. After the mixture was stirred for an appropriate time at an ambient temperature, the products were analyzed by GLC or isolated using silica gel column chromatography with hexane. The isolated products were analyzed by means of IR, ^{1}H NMR, and GC–MS spectroscopies.

The reactions under the strictly degassed conditions were performed using a reaction tube having a glass-tube branch or a quartz cell branch for absorption spectral measurement. The freeze–pump–thaw cycles (five times) were carried out. The reaction was started by mixing solid $NaBH_4$ in a tube with the mixture of (TPP)$Fe^{III}Cl$ and styrene in solvent in another tube.

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