Hydrogenation Catalysis by an Iron Porphyrin and Its Application to α,β-Unsaturated Esters

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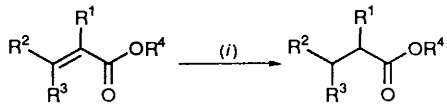
Chloro(5,10,15,20-tetraphenylporphyrinato)iron(III) in tetrahydrofuran–methanol catalysed the hydrogenation of α,β-unsaturated esters by $NaBH_4$ to the saturated esters; turnovers of up to 4580 h^{-1} have been attained for the hydrogenation of ethyl 2-methylbut-2-enoate. Deuterium labelling studies showed that the H^- of $NaBH_4$ and the H^+ of MeOH add to the β- and α-carbons of the double bond. A slower hydrogenation of oct-1-ene was accompanied by isomerization to oct-2-enes. Spectroscopy (UV/VIS, ^1H NMR and ESR) suggests that hydrogenation proceeds *via* an iron(II) intermediate, and an alkyl-iron(II) species seems likely.

Metalloporphyrin–reductant systems perform interesting hydrogenation reactions;[1] for instance, hydrogenations of alkyne,[2] styrene[3,4] and anthracene,[5] reduction of ketone to alcohol,[6] formation of dichlorocarbene, alkyl and alkenyl complexes of Co(tpp) and Fe(tpp) from carbon tetrachloride, alkene and alkyne (H_2tpp = 5,10,15,20-tetraphenylporphyrin),[7] reductive cleavage of S–O, S–N and S–C bonds in sulfoxides and sulfilimines,[8] reductive addition of thiophenol to styrene,[4a] and reduction of NO[9] and nitrobenzene.[10] All these reactions clearly indicate that such systems are potentially useful as hydrogenation catalysts, and motivated us to find an efficient hydrogenation catalyst.

In our preliminary work,[11] iron porphyrin-catalysed hydrogenation of ethyl 2-methylbut-2-enoate (ethyl tiglate, **1a**) was reported as a typical example of catalytic hydrogenation by a metalloporphyrin.† We report here a more detailed investigation of this hydrogenation catalysis (see Scheme 1 for reactions examined). The emphasis here, and the point of departure from the previous work,[11] lies in (1) informative results on intermediates, (2) significant acceleration of the catalytic hydrogenation by addition of methanol to the solvent and (3) a clear explanation of the latter effect. We also report efficient hydrogenation catalysis by an iron complex because descriptions of such catalysis are sparse.[12]

Experimental

Materials.—Chloro(5,10,15,20-tetraphenylporphyrinato)-iron(III), [Fe(tpp)Cl], was synthesised from tpp and $FeCl_3$ in acetic acid, followed by recrystallization from CH_2Cl_2–MeOH.[13] Its purity was confirmed by elemental analysis. Ethyl cyclohex-1-ene-1-carboxylate **1b** and ethyl 2,3-dimethylbut-2-enoate **1d** were synthesised by literature methods.[14,15] Commercially available **1a**, ethyl 3-methylbut-2-enoate **1c**, methyl *trans*-3-phenylprop-2-enoate (*trans*-methyl cinnamate) **1e**, oct-1-ene **3**, tetrahydrofuran (thf), bis(2-methoxyethyl) ether (diglyme), dimethylformamide (dmf) and methanol were dried by appropriate methods and distilled under a nitrogen atmosphere. Commercially available $NaBH_4$ (Nacalai tesque) and $NaBD_4$ (Aldrich) were used as received.



1 **2**

	R1	R2	R3	R4
a	Me	Me	H	Et
b	$(CH_2)_2$		H	Et
c	H	Me	Me	Et
d	Me	Me	Me	Et
e	H	Ph	H	Me

Scheme 1 (i) [Fe(tpp)Cl], $NaBH_4$

Reaction and Analysis.—*Catalytic hydrogenation of α,β-unsaturated esters.* A thf (or diglyme) solution of [Fe(tpp)Cl] was prepared by placing the complex in a flask equipped with a three-way stopcock, purging the air in the flask by several cycles of evacuation and introducton of N_2 and then injecting thf (or diglyme) with a syringe under a nitrogen atmosphere. The solution of the liquid substrate was prepared by injecting the substrate and solvent using syringes into a pre-purged flask under a nitrogen atmosphere. A typical reaction solution was prepared by putting $NaBH_4$ (2.0×10^{-3} mol) in a flask fitted with a three-way stopcock, flushing as described above, injecting a thf (or diglyme) solution (5.0 cm^3) of ethyl tiglate **1a** (1.0×10^{-3} mol) and *m*-xylene (an internal standard for GLC analysis), MeOH (1.0 cm^3) and the thf (or diglyme) solution (4.0 cm^3) of [Fe(tpp)Cl] (2.0×10^{-7} mol) with syringes under a nitrogen atmosphere. The reaction was carried out at 30 °C under a nitrogen atmosphere with stirring, and small aliquots were withdrawn at appropriate times to analyse the reactant and product by GLC [a packed column of Tween 80 (2 m) or an OV-17 capillary column (25 m)]. Anaerobic conditions were employed in preparing all the solutions described below. The hydrogenation of compound **1a** {[Fe(tpp)-Cl]:**1a**:$NaBH_4$ = 1:500:10 000, [Fe(tpp)Cl] = 2.0×10^{-5} mol dm^{-3}} was carried out at 30 °C in diglyme–MeOH (9:1) under anaerobic conditions achieved through three freeze–pump–thaw cycles. This reaction yielded rather smaller turnovers (1980 after 1 h) than in the usual anaerobic conditions (see Table 2). Thus, the latter method is preferred.

Deuteriation of ethyl tiglate **1a**. Compound **1a** was deuteriated with either $NaBH_4$ in thf–CD_3OD (9:1) or $NaBD_4$ in thf–MeOH (9:1). The same procedure and reaction

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† We described our work as the first report of metalloporphyrin-catalysed hydrogenation of a C=C double bond. However, we had missed several previous reports[2–4] on catalytic hydrogenation of a C=C double bond.

Table 1 Hydrogenation of α,β-unsaturated esters catalysed by NaBH$_4$–[Fe(tpp)Cl][a]

Substrate	Molar ratio substrate : complex	Turnover number
1a	5000[b]	2480
	600	600
1b	600	410
1c	600	67
1d	400	84
1e	600	54

[a] [Complex] = 4.0×10^{-5} mol dm^{-3} in diglyme–MeOH (9 : 1), substrate : NaBH$_4$ = 1 : 2, at 30 °C, 1 h. [b] In this reaction, [complex] = 2.0×10^{-5} mol dm^{-3} and complex : **1a** : NaBH$_4$ = 1 : 5000 : 10 000.

Table 2 Hydrogenation of ethyl tiglate **1a** catalysed by NaBH$_4$–[Fe(tpp)Cl]*

Solvent	Turnover number
thf–MeOH (9 : 1)	4580
diglyme–MeOH (8 : 2)	3090
diglyme–MeOH (9 : 1)	2480
diglyme–MeOH (24 : 1)	1100
dmf–MeOH (9 : 1)	580
diglyme	10

* [Complex] = 2.0×10^{-5} mol dm^{-3}, complex : **1a** : NaBH$_4$ = 1 : 5000 : 10 000, at 30 °C, 1 h.

conditions as described above were employed, except for a higher concentration of complex (2.0×10^{-4} mol dm^{-3}). After 1 h the solvents were evaporated at reduced pressure, and the residue dissolved in CDCl$_3$ (1.5 cm^3), which was subjected to ^{1}H NMR analysis.

*Reaction of oct-*1*-ene* **3**. In a pre-purged flask fitted up with a three-way stopcock and a condenser, [Fe(tpp)Cl] (1.25×10^{-5} mol), **3** (1.25×10^{-3} mol) and NaBH$_4$ (1.25×10^{-2} mol) in 5.0 cm^3 of solvent (thf–MeOH, diglyme–MeOH or diglyme) were allowed to react at 60 °C under a nitrogen atmosphere while being stirred. The products were analysed by GLC and GC–mass spectrometry [Shimadzu QP-1000, 70 eV (*ca.* 1.12×10^{-17} J)].

Measurements.—The UV/VIS spectra were recorded at about 30 °C with a Hitachi 150–20 spectrophotometer. The reaction solution was prepared by adding NaBH$_4$ (1000 equivalents) and compound **2a** (500 equivalents) to [Fe(tpp)Cl] (1.0×10^{-4} mol dm^{-3}) in a pre-purged flask, and then transferred to spectrophotometric cells (outside diameters = 1 and 10 mm) which were attached to the flask. All handling and measurements were performed under a nitrogen atmosphere. Proton NMR spectra were measured on samples prepared by dissolving the complex (1.0×10^{-2} mol dm^{-3}) in diglyme–CD$_3$OD in the same way as used to prepare the UV/VIS sample. A JEOL GX-400 spectrometer was used at 399.65 MHz, frequency 80 654.2 Hz, 25 °C. The ESR spectra were recorded at 77 K with a JEOL JES-FXAX spectrometer. The sample (1.0×10^{-3} mol dm^{-3} complex) was prepared in a flask fitted with an ESR tube, and then transferred to the ESR tube after five freeze–pump–thaw cycles.

Results and Discussion

The hydrogenation by NaBH$_4$ of ethyl tiglate **1a** in thf–MeOH (9 : 1) proceeds rapidly in the presence of [Fe(tpp)Cl] yielding ethyl 2-methylbutyrate **2a**, as shown in Fig. 1. Turnovers (moles of **2a** per moles of complex) up to 4580 are attained in 1 h, and the reaction is almost complete in 2 h, where [complex] = 2.0×10^{-5}, [**1a**] = 1.0×10^{-1} and [NaBH$_4$] = 2.0×10^{-1} mol dm^{-3} (complex : **1a** : NaBH$_4$ = 1 : 5000 : 10 000).

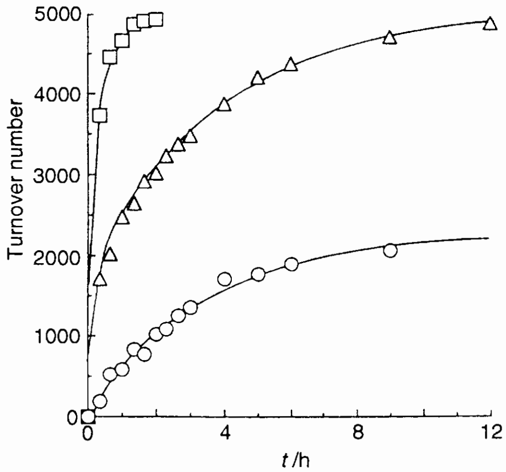

Fig. 1 Hydrogenation of compound **1a** by NaBH$_4$–[Fe(tpp)Cl]. Solvent: (□) thf–MeOH (9 : 1), (△) diglyme–MeOH (9 : 1), (○) dmf–MeOH (9 : 1). [complex] = 2×10^{-5} mol dm^{-3}, complex : **1a** : NaBH$_4$ 1 : 5000 : 10000, at 30 °C

Hydrogenation of **1a** does not proceed at all in the absence of the complex. Neither carbonyl reduction nor migration of the double bond occurs. This efficient hydrogenation catalysis is worthy of note, because such catalysis by iron complexes is rather rare.[12]

The reactivities of various α,β-unsaturated esters were examined in diglyme–MeOH (9 : 1). The α,β-disubstituted compound **1b** is hydrogenated rapidly as for **1a**, whereas β-disubstituted **1c** and **1d** are hydrogenated very slowly (Table 1). No side reaction occurs for **1b**–**1d** (the yields of **2b**–**2d** correspond to the consumption of **1b**–**1d**). In the case of *trans*-methyl cinnamate **1e**, however, the yield of **2e** is about a half of the consumption of **1e**, suggesting that some side reaction occurs (by-product unknown).

The catalytic activity of the complex depends significantly on the solvent used. Hydrogenation proceeds less rapidly in diglyme–MeOH (9 : 1) than in thf–MeOH (9 : 1), as shown in Fig. 1 and Table 2. Although it proceeds slowly in diglyme, addition of MeOH considerably accelerates the reaction; for instance, turnovers (in 1 h) increase from 10 (in diglyme) to 2480 by adding MeOH (10% v/v). The importance of MeOH is also clearly shown by the fact that an increase in its content leads to higher turnovers (Table 2). This acceleration by MeOH will be discussed below. Unexpectedly, the dmf–MeOH (9 : 1) solvent extremely suppresses the hydrogenation [compare dmf–MeOH (9 : 1) with thf–MeOH (9 : 1) in Table 2]. This result would arise from the fact that dmf can co-ordinate to the metal ion more strongly than can thf and diglyme; the donor number (kcal mol^{-1}, cal = 4.184 J) is 26.6 for dmf, 20.0 for thf and 19.2 for diethyl ether (the value for diglyme has not been reported).[16a] Co-ordination of dmf to Fe(tpp) would prevent either the formation of active species from [Fe(tpp)Cl] and BH$_4^-$ or the reaction of substrates with the active species.

Compound **1a** was deuteriated with NaBH$_4$ and the complex in thf–CD$_3$OD (Scheme 2),* to clarify the reason for methanol acceleration. The NMR signal of the α-hydrogen atom of ethyl 2-methylbutyrate (δ 2.23) is about 1/9 the intensity of that of the β-hydrogen atom (δ 1.33 and 1.53), indicating that ethyl 2-methyl[α-^{2}H]butyrate **3a**$^{\alpha D}$ is produced with a small concomitant yield of ethyl 2-methylbutyrate **3a** (molar ratio of **3a**$^{\alpha D}$: **3a** about 9 : 1). When compound **1a** is deuteriated with NaBD$_4$ and the complex in thf–MeOH the NMR signal of the β-hydrogen atom is about 1/4 the intensity of that of the α-hydrogen atom,

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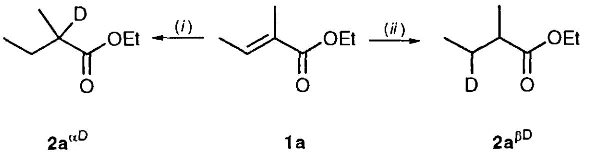
* Proton NMR spectroscopy shows that the signal of NaBH$_4$ does not decrease at all in the thf–CD$_3$OD solution clearly indicating that NaBH$_4$ undergoes no H–D exchange.

Table 3 Reaction of oct-1-ene **3** with $NaBH_4$ catalysed by [Fe(tpp)Cl][a]

		Product yield (%)		
			5[c]	
Solvent	Conversion of **3** (%)	**4**[b]	*cis*	*trans*
thf–MeOH (9 : 1)	37.3	12.4	5.4	1.2
diglyme–MeOH (9 : 1)	63.3	3.9	9.8	2.0
diglyme	39.7	2.0	4.7	0.8

[a] [Complex] = 2.5×10^{-3} mol dm^{-3}, complex : **3** : $NaBH_4$ = 1 : 100 : 1000, at 60 °C, 24 h. [b] Octane. [c] Oct-2-ene.



Scheme 2 (*i*) $NaBH_4$–[Fe(tpp)Cl], thf–CD_3OD; (*ii*) $NaBD_4$–[Fe(tpp)Cl], thf–MeOH

indicating that ethyl 2-methyl[β-^{2}H]butyrate **3a**^{βD} is formed as a major product (molar ratio of **3a**^{βD}:**3a** about 8:2). These results reveal that the H^- of $NaBH_4$ and the H^+ of MeOH are added to the β- and α-carbons of **1a**, and that MeOH accelerates the hydrogenation by supplying protons to the substrate. The methanolate anion is considered to build up as the hydrogenation proceeds. It is necessary to examine the effects of this anion and to use various protic solvents, in order further to elucidate the effects of methanol.

The [Fe(tpp)Cl]-catalysed hydrogenation of oct-1-ene **3** to octane **4** proceeds much more slowly than that of **1a**, accompanied by isomerization of **3** to *cis*- and *trans*-oct-2-enes **5** (Table 3). The sum of the yields is much lower than the consumption of **3**, suggesting some other reaction proceeds. However, no information on the other reaction is available at this moment. The low reactivity of the less-polar simple olefin **3** is not surprising, considering that the hydrogenation by this catalytic system proceeds *via* H^-/H^+ additions. The selectivity (hydrogenation *vs.* isomerization) depends on the solvent used: hydrogenation is predominant in thf–MeOH (9:1), but isomerization in diglyme–MeOH (9:1) and diglyme. To explain these results we consider first the reaction mechanism for the isomerization of **3**. Two mechanisms are commonly found in transition metal-catalysed isomerization of olefins:[17] one proceeds *via* an alkyl intermediate and the other *via* an η^3-allyl hydride intermediate. However, the latter seems unlikely here because it is difficult for the metalloporphyrin to supply three co-ordination sites, one for the hydride and two for the η^3-allyl ligand. On the other hand, the alkyl intermediate would be formed more easily than the η^3-allyl intermediate.* In fact, formation of alkyl iron porphyrins has been reported.[7,19] The dependence of the selectivity on solvent might be interpreted in terms of a common alkyliron intermediate through which hydrogenation and isomerization proceed.† The hydrogenation occurs if H^+ is added to the alkyliron species, but the isomerization occurs if the β-H atom of the alkyl group is abstracted by Fe. Protonation would be facilitated in polar solvents, since the MeO^- anion (one of the products of the protonation) would be stabilized by a polar solvent. Since diglyme–MeOH and diglyme are less polar than thf–MeOH (relative permittivity at 25 °C: MeOH, 32.66; dmf, 36.71; thf, 7.58; diglyme, 5.8[16b]) attack of H^+ on the alkyliron species is difficult in the former solvents, which favour isomerization. On the other hand, such attack occurs easily in the polar thf–MeOH solvent, which favours hydrogenation.

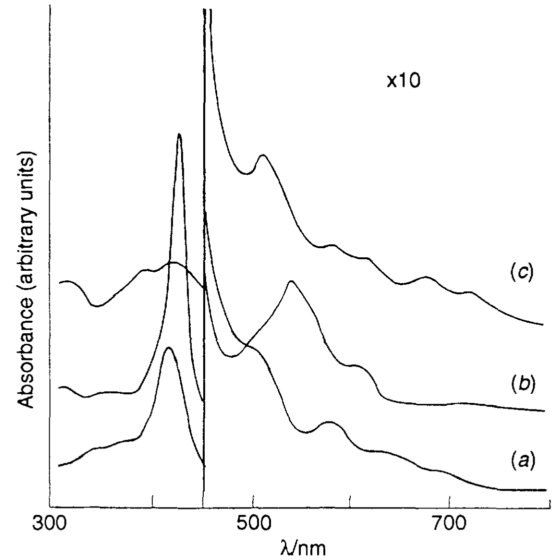


Fig. 2 The UV/VIS spectra of the catalytic system in thf–MeOH (9 : 1). (*a*) [Fe(tpp)Cl]; (*b*) complex : **1a** : $NaBH_4$ (1 : 500 : 1000) after mixing for 5 min; (*c*) complex : $NaBH_4$ (1 : 1000) and complex : **1a** : $NaBH_4$ (1 : 500 : 1000) after mixing for 1 h

In thf–MeOH (9 : 1), [Fe(tpp)Cl] shows the spectrum in Fig. 2(*a*) [λ_{max} = 340(sh), 375(sh), 416, 500(sh), 577, 625(sh), 680(sh) nm], which is similar to that of [Fe(tpp)(OMe)].[20] Upon mixing compound **1a** and $NaBH_4$ (complex : **1a** : $NaBH_4$ = 1 : 500 : 1000) the spectrum in Fig. 2(*b*) [λ_{max} = 426, 537, 552(sh), 600(sh) nm] is obtained, similar to that of [Fe(tpp)(thf)$_2$].[21] During the hydrogenation of **1a**, the UV/VIS spectrum of the catalytic system does not change from that of Fig. 2(*b*), and then changes to (*c*) [λ_{max} = 324, 365(sh), 394, 424, 511, 575(sh), 605(sh), 668, 712 nm] after the complete consumption of **1a** (after 1h). This spectrum is similar to that of $[Fe(tpp)]^-$.[22] Corresponding to these changes in the UV/VIS spectra, the ESR spectrum [Fig. 3(*a*), g = 5.8] of the high-spin iron(III) porphyrin immediately disappears upon mixing **1a** and $NaBH_4$ (complex : **1a** : $NaBH_4$ = 1 : 500 : 1000), yielding a very small signal of $[Fe(tpp)]^-$ at $g_\perp = 2.32$ and $g_\parallel = 1.95$ [Fig. 3(*b*)].[22] The ESR spectrum of the iron(I) species considerably enlarges after the complete consumption of **1a** (after 1 h), as shown by Fig. 3(*c*). These results indicate that the catalytic system mainly involves an ESR-silent iron(II) complex, and that this species is reduced to $[Fe(tpp)]^-$ after the complete consumption of **1a**. Such stepwise reduction of the complex by $NaBH_4$ also occurs more rapidly in the absence of **1a**; for instance, the ESR spectrum of the iron(I) species significantly enlarges after mixing the [Fe(tpp)Cl] and $NaBH_4$ for 10 min. When oxygen gas was introduced into the solution of $[Fe(tpp)]^-$ {the reaction mixture of [Fe(tpp)Cl] : **1a** : $NaBH_4$ 1 : 500 : 1000 in thf–MeOH (9 : 1) after 1 h}, [Fe(tpp)(thf)$_2$] was recovered in 86% (UV/VIS spectroscopic) yield based on the starting complex after 35 min, and Fe^{III}(tpp) was recovered in 87% yield[23] after 45 min.

Also in diglyme–MeOH (9 : 1), the ESR spectrum of [Fe(tpp)Cl] immediately disappears upon mixing **1a** and $NaBH_4$ (complex : **1a** : $NaBH_4$ = 1 : 500 : 1000), but that of the

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* Insertion of a C=C bond into a M–H bond generally proceeds *via* a four-centre transition state. A similar intermediate (or transition state), M–O–C–C, has been postulated in the epoxidation of olefins by oxometalloporphyrins,[18a,b] suggesting that the insertion of a C=C bond into the M–H bond is possible in metalloporphyrins. However, there is another possible pathway to form the iron–alkyl species. This is an electron transfer from the reduced iron species to the olefin followed by protonation. A similar radical intermediate has been proposed in the epoxidation of olefin by oxometalloporphyrin.[18c,d] At this moment we are not able to say which pathway is correct.

† The yield of *cis*- exceeds that of *trans*-oct-2-ene, contrary to the thermodynamic equilibrium. This result is consistent with the finding that olefin isomerization *via* a metal–alkyl intermediate generally yields more of the *cis* than of the *trans* form.[17]

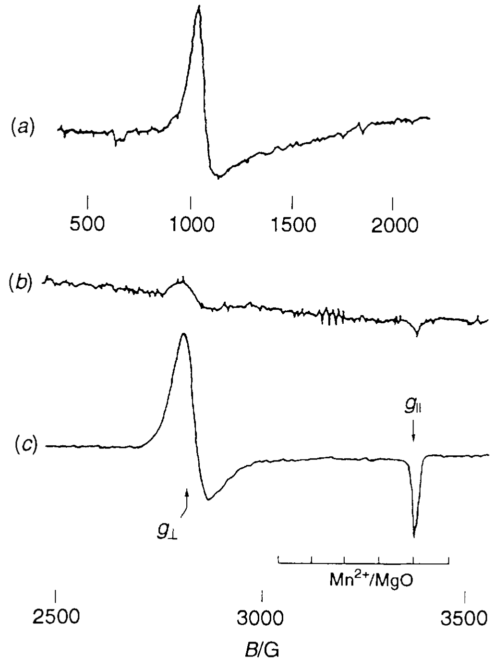

Fig. 3 The ESR spectra of the catalytic system in thf–MeOH (9:1). Details as in Fig. 2; G = 10^{-4} T

iron(I) species does not appear even after the complete consumption of **1a**. The UV/VIS spectrum of [Fe(tpp)Cl] [Fig. 4(*a*)] changes to that in Fig. 4(*b*) on adding $NaBH_4$ in small excess (5 equivalents with respect to the complex). This spectrum is similar to that of $[Fe(tpp)(thf)_2]$.[21] Consistent with this change, the ^1H NMR spectrum of the [Fe(tpp)Cl]–$NaBH_4$ (1:1) system clearly shows that high-spin $[Fe(tpp)L_2]$ (L = diglyme) is formed in diglyme–CD_3OD (9:1) [Fig. 5(*a*): δ 49 (β-H of pyrrole), 8.5 (*o*-H of *meso*-Ph) and 7.6 (*m*- and *p*-H of *meso*-Ph)].[24] The UV/VIS spectrum in Fig. 4(*b*) further changes to (*c*) (λ_{max} = 308, 364, 426, 504, 610, 714 nm) upon addition of a large excess of $NaBH_4$ (1000 equivalents to the complex). This spectrum differs from that of $[Fe(tpp)(thf)_2]$.[21] The proton NMR spectrum also significantly changes upon adding $NaBH_4$ in large excess (200 equivalents to complex), as shown in Fig. 5(*b*) [δ 28 (β-H of pyrrole), 14 (*o*-H of *meso*-Ph), 9.6 (*p*-H of *meso*-Ph), 7.2 (*m*-H of *meso*-Ph)]. This spectrum differs from that of the diamagnetic species.[25] The spectrum in Fig. 5(*b*) cannot be explained by the formation of the iron(I) species since [Fe(tpp)Cl] cannot be reduced to $[Fe(tpp)]^-$ by $NaBH_4$ in diglyme–MeOH (see above), suggesting the formation of some new iron(II) species. This spectrum cannot be assigned to $[Fe(tpp)H]^-$ which is considered to be diamagnetic (as are similar metalloporphyrin species[26,27]). Addition of **1a** (500 equivalents to complex) to the complex: $NaBH_4$ = 1:1000 system yields the spectrum in Fig. 4(*d*) which is similar to that of a basket-handle tetraphenylporphyrin involving two $(CH_2)_{12}$ chains bound through an ether linkage to the *ortho* positions of two opposite phenyl rings, the cross-*trans* linked isomer, with one chain over and the other under the porphyrin ring.[26] These results strongly suggest that the α,β-unsaturated ester reacts with some active species which is formed by adding the large excess of $NaBH_4$ to [Fe(tpp)Cl], yielding $[Fe(tpp)R]^-$.* This suggestion accords with the very recent reports by Kano *et al.*,[4c] in which $[Fe(tpp)R]^-$ is proposed as an intermediate in the catalytic hydrogenation of styrene by the [Fe(tpp)Cl]–$NaBH_4$ system.

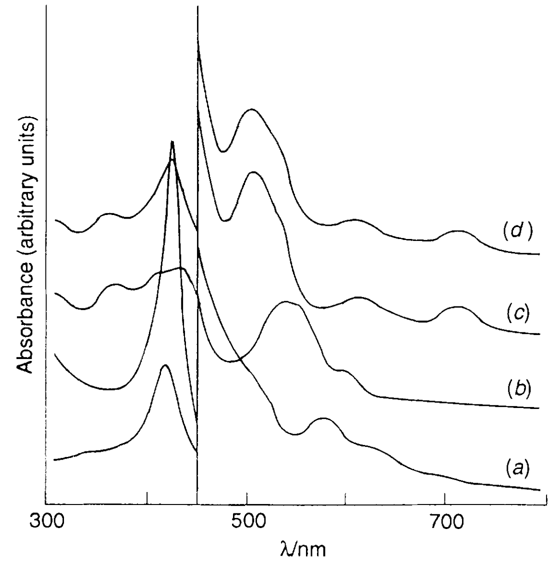

Fig. 4 The UV/VIS spectra of the catalytic system in diglyme–MeOH (9:1): (*a*) [Fe(tpp)Cl]; (*b*) complex:$NaBH_4$ (1:5); (*c*) complex: $NaBH_4$ (1 : 1000) and complex:**1a**:$NaBH_4$ after mixing for 1 h; (*d*) complex:**1a**:$NaBH_4$ (1:500:1000) after mixing for 5 min

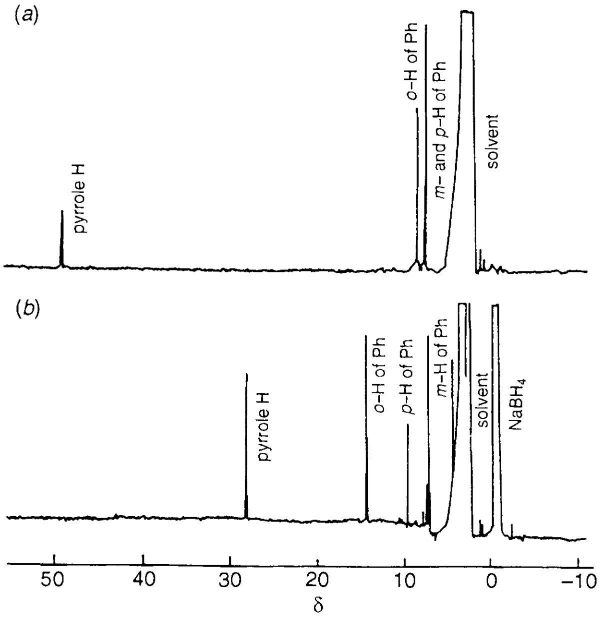

Fig. 5 Proton NMR spectra of the catalytic system in diglyme–CD_3OD (9:1). [Fe(tpp)Cl]:$NaBH_4$ = 1:1 (*a*) and 1:200 (*b*)

Here, we discuss briefly the low reactivity of oct-1-ene. The UV/VIS spectrum of [Fe(tpp)Cl]–$NaBH_4$ in diglyme–MeOH (9:1) changes little upon addition of oct-1-ene, but considerably upon addition of ethyl tiglate. These results suggest that it is difficult for oct-1-ene to react with the active species and to yield the intermediate.

In thf–MeOH (9:1) only $[Fe(tpp)(thf)_2]$ is spectroscopically observed unlike in diglyme–MeOH (9:1). This difference is not surprising; in the polar thf–MeOH solvent the protonation of the anionic alkyliron(II) porphyrin would proceed rapidly (MeO^-, one of the products of protonation, would be easily formed in polar solvents). Accordingly, the alkyliron(II) porphyrin would be immediately converted to $[Fe(tpp)(thf)_2]$

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* We failed to observe the NMR spectrum of $[Fe(tpp)R]^-$: the spectrum in Fig. 5(*b*) changes very little upon addition of an excess of **1a** (100 equivalents to complex) to the complex:$NaBH_4$ 1:200 mixture probably because all of **1a** would be consumed before the measurement owing to the high complex concentration (1.0×10^{-2} mol dm^{-3}), much higher than 2.0×10^{-5} mol dm^{-3} employed in the catalytic system. Further experiments need to be carried out at low temperature, using a low methanol content.

with formation of the hydrogenated product in the thf–MeOH. Actually, the hydrogenation in thf–MeOH proceeds much more rapidly than in diglyme–MeOH (see above), probably due to facile protonation in the former solvent. Similar behaviour has been observed in the reaction of oct-1-ene **3**, where hydrogenation is predominant in thf–MeOH due to rapid protonation, but isomerization is dominant in diglyme–MeOH owing to slow protonation.

In summary, an active species is formed from [Fe(tpp)Cl] by adding a large excess of $NaBH_4$. This species differs from $[Fe(tpp)(thf)_2]$, but detailed information could not be obtained. The α,β-unsaturated ester and alkene react with the active species to yield an iron(II) intermediate, possibly $[Fe(tpp)R]^-$. This intermediate undergoes protonation by MeOH, yielding the hydrogenated product.

Finally, we would like to discuss the differences between our results and those of Setsune *et al.*[7d,e] who carried out similar experiments. In the case of Setsune *et al.*, an alkyliron(III) porphyrin is formed from [Fe(tpp)Cl], alkene and $NaBH_4$. In our case, an iron(II) and even an iron(I) porphyrin are formed, and catalytic hydrogenation proceeds. These differences would arise from the different reaction conditions. In the experiments of Setsune *et al.* toluene–MeOH (40:1) was employed as solvent and the molar ratio of complex:alkene:$NaBH_4$ was 1:70:70 ([complex] = 2.0×10^{-2} mol dm^{-3}). We employed thf–MeOH (9:1) and diglyme–MeOH (9:1) as solvents and the molar ratio of complex:**1a**:$NaBH_4$ was 1:5000:10 000 ([complex] = 2.0×10^{-5} mol dm^{-3}). Under our conditions there seems to be enough $NaBH_4$ to carry out the reduction of [Fe(tpp)Cl] and hydrogenation of a C=C double bond. Under the conditions of Setsune *et al.* the hydrogenation of **1a** by $NaBH_4$ catalysed by [Fe(tpp)Cl] yields small turnovers (2.4 after 1 h). In other words, our conditions are favourable for reduction of [Fe(tpp)Cl] and hydrogenation of a C=C double bond, whereas those of Setsune *et al.* are favourable for the formation of an alkyliron(III) porphyrin.

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