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Preliminary communication

σ-BONDED METHYLIRON PORPHYRINS? THE CONVERSION OF IRON(III) TO MAGNESIUM(II) PORPHYRINS BY METHYL-GRIGNARDS

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Summary

Iron(III) porphyrins react with methyl-Grignard reagents to produce in sequence two similar but distinct $S = 1$ iron(II) porphyrins followed by the magnesium(II) complex. Stable porphyrin alkylirons are not produced by the methyl-Grignards, methyllithium, or sodium cyclopentadienide.

The reaction of alkyl-Grignard reagents with iron(III) porphyrins is now considered a general method for the preparation of σ-bonded porphyrin alkylirons [1] (eq. 1). However, the original report of an etioporphyrin ethyliron derivative [2] emphasized the instability of such species. An NMR spectrum could not be taken. Moreover, the existence of only a fleeting octaethylporphyrin allyliron species has been deduced from visible spectra [3a]. In an effort to examine the chemistry of porphyrin alkylirons we have sought to prepare the methyl derivatives by literature procedures. The Grignard procedure seemed most direct and has been successful with the more stable aryl derivatives [3]. We find, however, that the reaction of iron(III) porphyrins with methyl-Grignard reagents does not produce alkylirons but rather generates in sequence two similar but distinct iron(II) porphyrins of intermediate spin followed by formation of the magnesium complex.

$$\mathrm{PFe^{III}Y} \xrightarrow{\mathrm{RMgX}} \mathrm{PFe^{III}R} + \mathrm{MgXY} \qquad (1)$$

$(Y = Cl, ClO_4, X = Cl, Br, I)$

Following the procedure of Cocolios and colleagues [1] we find the reaction of 0.001 *M* chloroiron(III) octaethylporphyrin with methylmagnesium bromide in dry toluene under argon generates the red solution ascribed to the $FeCH_3$ species ($PFe^{II}a$, Fig. 1) but in fact entails the visible spectral changes shown in

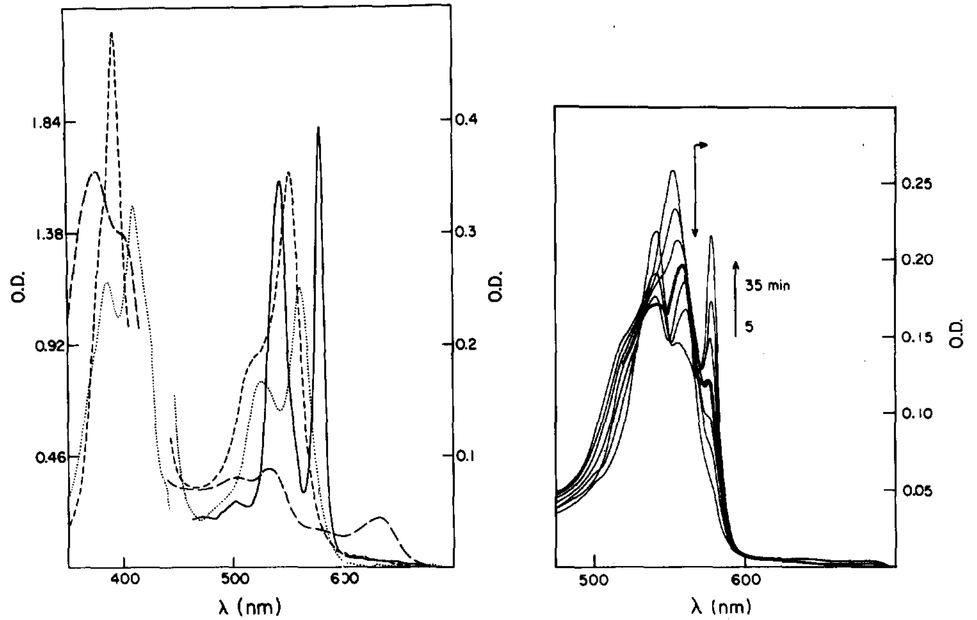

Fig. 1(a). Visible spectra of octaethylporphyrin complexes in toluene (0.01 cm cell): $PFe^{III}Cl$ (— —) 1.8×10^{-3} *M*; $PFe^{II}a$ (- - -) 1 min after addition of CH_3MgBr, 0.021 *M*; $PFe^{II}b$ (· · ·) after 21 h; PMg^{II} (——) 16.5 h after treatment with 0.21 *M* CH_3MgBr (off scale soret not shown). (b) Repeat scan of reaction with 0.21 *M* CH_3MgBr at 5 to 35 min; (▬) at 20 min.

Figure 1. For Figure 1a different concentrations of Grignard reagent and different times were chosen to illustrate each component of the mixture. A partial repeat scan of a single reaction solution at the higher concentrations of Grignard reagent is shown in Fig. 1b. Clearly the initial spectrum is dependent upon the initial concentration of reagent. The first step in the process, observed at low or stoichiometric levels of reagent, is an electron transfer from methyl-Grignard to iron(III) porphyrin. This results in an iron(II) porphyrin ($PFe^{II}a$) and a methyl radical. The latter in toluene produces methane and ethane quantitatively (eq. 2). The visible spectrum of $PFe^{II}a$ corresponds exactly to the spectrum assigned the methyliron structure.

$$CH_3MgBr + ClFe^{III}P \xrightarrow[\text{Ph–CH}_3]{} PFe^{II}a + \underset{(95\%)}{CH_4} + \underset{(5\%)}{C_2H_6} \qquad (2)$$

The rapidly first-formed iron(II) complex reacts with Grignard reagent to form a second heme ($PFe^{II}b$). The latter is converted to the magnesium(II) porphyrin by the reagent. The general sequence, and rate constants (l mol^{-1} sec^{-1}) for the last two steps are sketched in eq. 3 (P = octaethylporphyrin).

$$PFe^{III}Cl \xrightarrow[\text{very fast}]{CH_3MgBr} PFe^{II}a \xrightarrow[k\,=\,6.8 \times 10^{-3}]{CH_3MgBr} PFe^{II}b \xrightarrow[k\,=\,1.7 \times 10^{-3}]{CH_3MgBr} PMg^{II} \qquad (3)$$

Both air sensitive hemes form diamagnetic carbonyl and bis-*N*-methylimidazole or bis-pyridyl adducts that are identical. Both are demetallated under argon

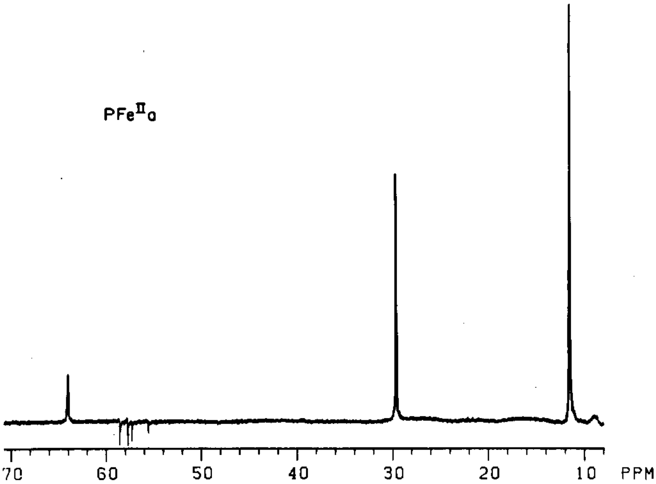

Fig. 2. 300 MHz NMR spectrum of heme a in toluene.

with trifluoroacetic acid to octaethylporphyrin. Moreover, both show the same NMR spectrum [4a] (Fig. 2). It is characteristic of $S = 1$ iron(II) octaethylporphyrin [4b]. The spectrum in Fig. 2 is that of a solution containing both CH_3MgBr and CH_3I. The protons for these at δ −1.5 and 2.2 are not shown. Visible spectra were taken before and after the NMR data was gathered to be sure each species was intact.

Heme b can be converted back to heme a by treatment with excess methyl iodide, or bromide. Thus, the two hemes are interconvertible (eq. 4).

$$\mathrm{PFe^{II}b} \underset{\mathrm{CH_3MgX}}{\overset{\mathrm{CH_3X}}{\rightleftarrows}} \mathrm{PFe^{II}a} \tag{4}$$

The reactivity, NMR and visible spectra of PFe^{II}a generated by the addition of methyl halide to heme b or that originally formed by the Grignard reagent are the same. Moreover, the spectrum of these solutions does not change upon addition of deaerated water. Thus, we presume PFe^{II}a is an alkyl halide solvate of an $S = 1$ iron(II) porphyrin generated by excess CH_3X present in the reagent. Some other component of the Grignard solution may also elicit the visible spectral changes observed.

We have recently found that deuteroheme in basic isopropanol/water reversibly complexes with simple methyl halides [5]. The adducts are $S = 1$ iron(II) porphyrins and the visible spectrum is nearly identical with that shown in Fig. 1 for PFe^{II}a. The same kind of complex could explain the observations herein (eq. 5).

$$\begin{tikzcd} \mathrm{PFe^{III}Cl} \arrow[r, "\mathrm{CH_3MgX}"] & \mathrm{PFe^{II}} \arrow[r, shift left, "\mathrm{CH_3X}"] \arrow[d, "\mathrm{CH_3MgX}"] & \mathrm{PFe^{II}(CH_3X)} \arrow[l, shift left, "\mathrm{CH_3MgX}"] \\ & \mathrm{PMg^{II}} & \end{tikzcd} \tag{5}$$

Reaction 5 also explains the rather temperamental spectral observations typical of these reactions [6].

The conversion of chloro or perchlorato iron(III) to iron(II) porphyrin is apparently a general reaction of group I and II organometals. The transformation (with tetraphenylporphine or octaethylporphyrin) can be accomplished smoothly with sodium cyclopentadienide, methyllithium, or methylmagnesium iodide, bromide or chloride. The spectra of the iron(II) porphyrins ($PFe^{II}b$) are identical to those obtained by reduction with $NaBH_4$. Whether the process in eq. 2 entails an unstable iron-methyl or proceeds by an outer sphere mechanism is unknown. Clearly, related solution structures [7] assigned on the basis of visible spectra and method of preparation should be reconsidered.

Magnesium and iron-porphyrins play a dominant role in the light gathering and redox processes of living systems. Thus, the apparently simple iron(III) to magnesium(II) metal exchange noted herein warrants further investigation.

Acknowledgement

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