Unexpected Alkyl Complex Formation and Correlation of Porphyrin Bascity with Alkyliron(III) Homolytic Stability

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The σ-bonded alkyl and aryliron(III) porphyrins are usually obtained from the reaction of the chloroiron(III) porphyrin with Grignard reagents or alkyllithium.[1] An alternative route involves reaction of the iron(I) porphyrin anion derivative with alkyl halides. The resulting (Por)Fe(III)R (R=alkyl, aryl) complexes exist as pentacoordinate, low-spin($S=1/2$) iron(III) complexes in noncoordinating solvents.[2]

This work addresses examination of relative stabilities of alkyliron(III) porphyrins depending upon the phenyl ring substituents and verification of unexpected alkyl aroup transfer from triethylborohydride to chloroiron(III) porphyrin, which may provide another route for formation of the alkyl complexes of iron(III) porphyrins.[3] The reaction was discovered in attempts to make unprecedent hydride iron porphyrin complexes. The NMR (Bruker WM-360 FT) methodology was used here to detect the products of the triethylborohydride reaction, and to monitor the relative stabilities of ethyliron(III) tetraarylporphyrins as a function of aryl substitutents of a β-pyrrole resonance of Fe(II) product in case of fluorinated phenyl iron porphyrins. Ethyliron(III) porphyrin complex was prepared both by stoichiometric addition of $NaEt_3BH$ to a solution of (Por)Fe(III)Cl and by combination of $NaEt_3BH$ and sulfur with a 2.0-6.0 mM solution of (Por)Fe (III)Cl at room temperature.

Addition of 1.0 equiv. of $NaEt_3BH$ in THF to toluene solutions of chloroiron(III) porphyrins results in ethyl complex formation with a corresponding β-pyrrole proton resonance ranging from -17.5 ppm to -20.05 ppm as prophyrin phenyl substitutents are varied from para-methoxy to pentafluoro. The β-methyl resonance of the coordinated ethyl group ranges from -115 ppm to -126 ppm due to porphyrin substituent effects. At room temperature chemical shift of β-pyrrole and a coordinated β-methyl for (p-OCH_3)Fe(III)Et are -17.5 and -115 ppm, for (TPP)Fe(III)Et are -17.6 and -117 ppm, for (F_8-TPP)Fe(III)Et are -19.5 and -124 ppm, and for (F_{20}-TPP)Fe(III)Et are -20.1 and -126 ppm, respectively. The ethyl α-methylene porton resonance is not seen (located at 554 ppm) in the ^1H-NMR spectrum due to large linewidth.[4]

The triethylborohydride reagent also serves as a reducing agent, and variable amounts of iron(II) products are seen along with the alkyliron(III)porphyrin. In the 0.4% THF-toluene reaction medium the iron(II) exists as a mixture of square-planar $S=1$ and THF-ligated $S=2$ species in rapid exchange. The resulting pyrrole phenyl protons are in the downfield region, and the chemical shift values are sensitive to the iron(II) prophyrin/THF ratio and phenyl substituents. Use of substoichiometric quantities of triethylborohydride anion also produces both ethyliron(III) and iron(II) products. Equivalent results were obtained with the $LiEt_3BD$ analogue.

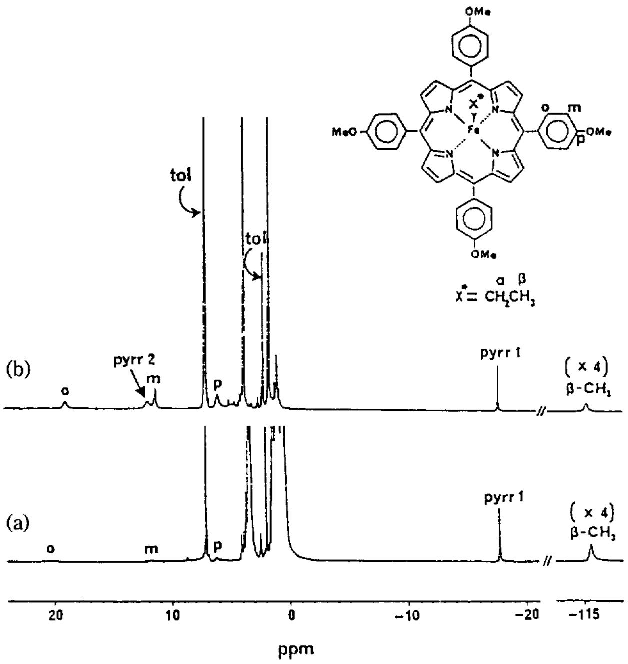

Figure 1. Proton NMR spectra of ethylion(III); porphyrin, 360 MHz, at 298 K. The pyrrole signal of ethyliron(III) porphyrin complex is denoted "pyrr 1", coordinated methyl proton signal "-CH_3". The pyrrole and phenyl proton resonances for (p-OCH_3) TPPFe(II)(THF)X as "pyrr 2", "ortho as o", "meta as m", and "para methoxy as p". (a) reproduced result of ref. 8 with concentration of 4 mM. (b) addition of 1.0 eq. $NaEt_3BH$ to a toluene solution of (p-OCH_3)TPPFe(III)Cl with concentration of 2 mM.

Ethyliron(III) prophyrins are relatively unstable, and several hours after generation the ratio of iron(II) to ethyliron(III) porphyrin increases, presumably as a result of Fe-C bond homolysis. Porphrins with different basicities were examined and we varied phenyl ring substitutents from electron-releasing OCH_3 group to electron-withdrawing group such as F. The apparent half life for Fe-C bond homolysis is on the order of day for (p-OCH_3)TPPFe(III)Et, TPPFe(III)Et and with a qualitative decrease in stability. The (F_{20}-TPP)Fe(III) Et shows a remarkably short half life of 45 minutes. Hence, the relatively electron-deficient iron prophyrins show the greatest tendency to give the ultimate iron(II) homolysis product. This is surprising in that the electron-deficient iron(III) porphyrins have a higher affinity for axial ligand coordination. We initially expected that electron-deficient porphrins would have a higher affinity than less electron-deficient porphrins. However the opposite result was obtained, which can be explained by the extent of iron(II) porphyrin stabilization. The electron-withdrawing substituents in the porphyrin-phenyl ring stabilize the iron(II) by delocalization through conjugated macrocycle. An explanation for this apparent discrepancy for effective homolysis may be found in the relative stabilization of the iron(II) product. Hence a variety of evidences suggest homolysis is reversible[5-7]: (TPP)Fe(III)-R$\rightleftarrows$(TPP)Fe (II)+R·.

Homolysis of the Fe-C depending on ring basicity

Types of porphyrins	Half life for Fe-C homolysis
$(F_{20}\text{-TPP})\text{Fe(III)Et}$	45 min.
$(F_8\text{-TPP})\text{Fe(III)Et}$	2 days
TPPFe(III)Et	3.5 days
$(p\text{-OCH}_3)\text{TPPFe(III)Et}$	4 days

$*(\text{Por})\text{Fe(III)Cl} + \text{NaEt}_3\text{BH} \xrightarrow{\text{tol}} (\text{Por})\text{Fe(III)Et}$

F_{20}-TPP: dianion of tetrakis (pentafluorophenyl) porphyrin

F_8-TPP: dianion of tetrakis (*o,o'*-fluorophenyl) porphyrin

TPP: dianion of tetrakis (tetraphenyl) porphyrin

(p-OCH_3)TPP: dianion of tetrakis (p-methoxyphenyl) porphyrin.

Diminished reactivity of the iron(II) product for electron deficient iron(II) porphyrins would slow the reverse reaction and cause loss of R· by disproportionation, coupling, solvent hydrogen atom abstraction, etc. Alkyl complex formation is verified from carbon monoxide insertion reaction, which ended up to forming (F_{20}-TPP)Fe(II)CO complexes at 8.8 ppm and (F_{20}-TPP)Fe(III)C(=O)CH_2CH_3 complex formation at −10.5 ppm of characteristic pyrrole resonances, presumably *via* radical process. After injection of carbon monoxide at 1 atm for 10 seconds into a 5 mm NMR tube containing ethyl complex, the integrated signals of the products result in 91% (F_{20}-TPP)Fe(II)CO and 9% (F_{20}-TPP)Fe(III)C(=O)CH_2-CH_3. Resulting large portion of (F_{20}-TPP)Fe(II)CO complexes can be attributable to the square-planar (F_{20}-TPP)Fe(II) (85 %), which was already produced from Fe-C bond homolysis. A β-pyrrole resonance of electron-deficient (F_{20}-TPP)Fe(III) acyl complex shows upfield shift by 2.0 ppm as compared with that of TPPFe(III)C(=O)R with pyrrole at −8.6 ppm.[6] Another set of experiment was carried out by CS_2 insertion reaction into a possible alkyliron(III) porphyrin complex. Assuming the formation of alkyl porphyrin complex, the insertion product for CS_2 revealed the same result described elsewhere.[7] The product was a dithiocarboxylatoiron(III) porphyrin complex, TPPFe(III)CS(=S)CH_2CH_3. Reaction of (p-OCH_3) TPPFe(III)Cl with $NaEt_3BH$ was investigated further because product identification is not consistent with an earlier literature report.[8] Retrospective interpretation of other spectroscopic results[8] also points to the unusual alkyl group transfer to the iron(III) porphyrin.

The "strong g-max" EPR signal reported for the product[8] matches that known for low-spin alkyliron(III) porphyrins. Optical spectra are also consistent with the alkyliron(III) formulation. Optical spectra bands at 412 (soret), 523, and 612 nm resemble those for known alkyliron(III) tetraarylporphyrins. An ethyl group and SH^- are isoelectronic. A disordered ethyl group could well emulate SH^- ligand electron density in the reported crystal structure. A signal at 6.7 ppm assigned to the coordinated S-H group is not seen in our spectra. On the basis of r^{-6} dipolar relaxation (comarison with pyrrole proton linewidth) the S-H signal (*ca.* 1250 Hz) would not have been detected by high resolution NMR (360.13 MHz) due to large line broadness.

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