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Formation of the Tributyltin–Iron(III) Porphyrin Complex by a Free Radical Process

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Surprising and often unprecedented chemistry is evident for organometallic complexes of metalloporphyrins.[1] This is clearly the case for alkyl/aryl complexes of paramagnetic iron(III) porphyrins that exhibit the following atypical reactivities: (i) reversible migration of the alkyl/aryl ligand from the metal center to a porphyrin pyrrole nitrogen;[2] (ii) hydrometalation of alkynes to give σ-vinyliron(III) porphyrins;[3] (iii) "insertion" of dioxygen into the Fe–C bond of alkyl/aryl–iron(III) porphyrins to give a transient organic peroxide complex;[4] (iv) "insertion" of CO,[5,6] CO_2,[5] and SO_2[7] into the Fe–C bond of alkyliron(III) porphyrins; and (v) a novel alkyl group free radical "interchange" with alkyl halides.[8]

Mechanistic investigations of the CO "insertion" and alkyl group interchange reactions reveal a facile thermal homolysis of the Fe–C bond as an initial step.[5,6,8] The reverse reaction is nearly diffusion controlled on the basis of pulsed radiolysis measurements.[9]

$$(P)Fe^{III}{-}R \rightleftarrows (P)Fe^{II} + {}^{\bullet}R$$

The net result is that alkyliron(III) porphyrin solutions provide an ambient temperature, steady state source of free radicals. There is close analogy between the thermal homolytic process for alkyliron(III) porphyrins and that described for an alkylcobalt(III) macrocycle and termed the "persistent radical effect".[10,11] Eventual loss of the radical by combination, disproportionation, etc., means that the alkyliron(III) porphyrins are thermally unstable, and the iron(II) product appears over a period of hours or days dependent on the porphyrin ring basicity.

We reasoned that the alkyl radical should readily abstract a hydrogen atom from a trialkyltin hydride substrate, and indeed this report describes the consequences of addition of excess tributyltin hydride to solutions of alkyliron(III) porphyrins. Evidence is presented that the resulting tin radical then combines with the iron(II) porphyrin to generate an unprecedented paramagnetic (tributyltin)iron(III) porphyrin complex.[12] Results are consistent with the following sequence:

$$(P)Fe^{III}R \rightleftarrows (P)Fe^{II} + {}^{\bullet}R$$

$${}^{\bullet}R + Bu_3SnH \rightarrow RH + Bu_3Sn^{\bullet}$$

$$Bu_3Sn^{\bullet} + (P)Fe^{II} \rightleftarrows (P)Fe^{III}SnBu_3$$

Tributyltin hydride is capable of electron transfer, and the alkyliron(III) tetraphenylporphyrin complex is partially reduced to $(TPP)Fe^{II}$ in competition with the reactions cited above. Use of the more basic tetrakis(*p*-methoxyphenyl)porphyrin, *p*-OCH_3-TPP, suppressed the electron transfer reduction pathway. Gas evolution was apparent for the Bu_3SnH/(p-OCH_3TPP)FeR reaction mixture, and the product alkane (RH = propane or butane for R = propyl or butyl) was detected by GCMS. The reaction course was conveniently monitored by deuterium NMR spectroscopy (Figure 1) in which case the pyrrole-deuterated

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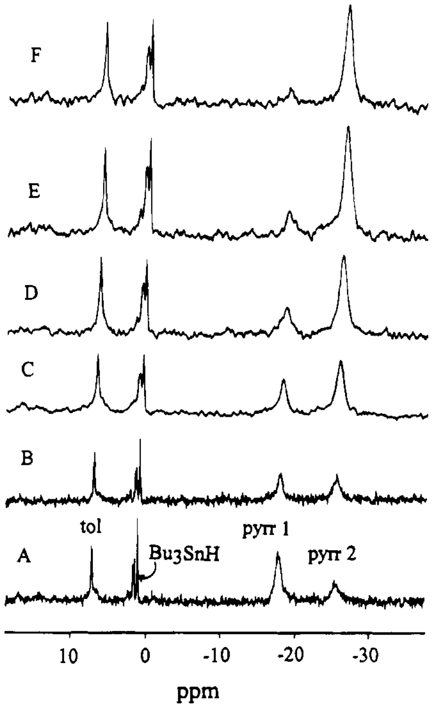

Figure 1. Deuterium NMR spectra (55 MHz) recorded during the reaction of excess Bu_3SnH (approximately 0.4 M) with pyrrole-deuterated (*p*-OCH_3TPP)FeBu (4 mM) in toluene solution at 25 °C, chemical shift values referenced to $(CD_3)_4Si$. Time after addition of excess Bu_3SnH: (A) 15 min; (B) 30 min; (C) 45 min; (D) 60 min; (E) 75 min; (F) 90 min. The pyrr 1 signal corresponds to the pyrrole deuteron signal of (*p*-OCH_3TPP)FeBu, and that of pyrr 2 to the product (*p*-OCH_3TPP)$FeSnBu_3$.

(*p*-OCH_3TPP)Fe compound was utilized. The alkyliron(III) derivative was generated in situ by the Grignard route under anaerobic conditions as previously described.[13] The pyrrole deuteron chemical shift value for the parent low-spin alkyliron(III) complex is −18.5 ppm. Deuterium NMR spectra recorded over a period of 90 min (25 °C) following addition of excess Bu_3SnH reveal growth of a new pyrrole signal at −25.2 ppm as seen in Figure 1. A pyrrole resonance in this upfield region is typical for low-spin iron(III) tetraarylporphyrin complexes.

The resulting red solution yielded an optical spectrum with bands at 412 (Soret), 532, and 606 nm (toluene solution) representative of low-spin iron(III) porphyrin complexes. Over a period of hours the new species spontaneously decomposed to the $S = 1$ iron(II) porphyrin. The tributyltin decomposition product was not identified, but presumably hexabutylditin is formed. Efforts to grow crystals of the new product with slow diffusion of heptane into the solution maintained at −25 °C yielded only crystals of the square-planar iron(II) derivative. When exposed to air the new tributyltin complex product was rapidly converted to the dinuclear μ-oxoiron(III) porphyrin. Light was not required to effect the tributyltin hydride reaction, and the resulting product was not particularly light sensitive.

Further evidence that the new low-spin iron(III) porphyrin species is the tributyltin complex comes from an independent preparative route. Lithium tributyltin ($LiSnBu_3$) was generated in THF at 0 °C by reaction of lithium diisopropylamide with tributyltin hydride.[14] Addition of 1.0 equiv of $LiSnBu_3$ to (*p*-OCH_3TPP)FeCl in toluene solution resulted in generation of a product with pyrrole proton and deuteron NMR signals at −25.2 ppm, identical to the signal produced from the tributyltin hydride reaction with the alkyliron(III) porphyrin complex. The $LiSnBu_3$ reagent is an effective reductant, and variable amounts of iron(II) porphyrin species were evident.

Proton NMR signals were assigned for the phenyl resonances of the putative (*p*-OCH_3TPP)$FeSnBu_3$ at 3.31 and 3.39 ppm for the phenyl meta protons and 2.06 and 2.57 ppm for the phenyl ortho protons. This splitting pattern for phenyl groups lying orthogonal to the porphyrin plane is typical of that for other five-coordinate alkyl- and silyliron(III) tetraarylporphyrin complexes.[13,15] The phenyl−OCH_3 signal was apparently obscured by the strong THF signals. Two additional resonances at 8.86 and 5.25 ppm were assigned respectively to the α- and β-CH_2 groups of coordinated $SnBu_3^-$ on the basis of line width and intensity with respect to the pyrrole proton signal. (The 3:4 CH_2/pyrrole proton signal intensity ratios imply a 1:1 stoichiometry.) The other butyl proton signals presumably lie under strong THF or solvent signals. Variable temperature proton NMR measurements revealed Curie law behavior (a linear plot of chemical shift vs $1/T$) for the pyrrole and α-CH_2 butyl signals, but the β-CH_2 signal moved upfield as the temperature was lowered. This apparent reversed-Curie behavior may be due to temperature-dependent conformational variation of the butyl methylene groups.

An estimated magnetic moment of $2.0 \pm 0.2\ \mu_B$ for the (*p*-OCH_3TPP)$FeSnBu_3$ complex was obtained by the NMR method in which corrections for the iron(II) porphyrin contaminant obtained from deuterium NMR integrations were applied. At liquid nitrogen temperature the EPR spectrum in frozen toluene solution also shows a characteristic low-spin iron(III) pattern with apparent g values of 2.43, 2.27, and 1.93.

An empirical trend is evident in the pyrrole chemical shift values for the (TPP)Fe−L series where the ligand contains a group (IV) element. Hence, for $L = -CH_2CH_3^-$, $-Si(CH_3)_3^-$, and $-SnBu_3^-$ the respective pyrrole proton chemical shift values are −17.9, −21.2, and −25.7 ppm (-25.2 ppm for (*p*-OCH_3-TPP)$FeSnBu_3$). This trend is inversely related to the magnitude of paramagnetic shifts for axial ligand protons. Values for Fe−C−CH_3, Fe−Si−CH_3, and Fe−Sn−CH_2^- are −117,[8] −1.2,[15] and +8.86 ppm[16] (values for alkyl and silyl complexes are for TPP and the value for the tin complex is for *p*-OCH_3TPP). As less unpaired spin is transmitted through the heavier group(IV) elements, more spin resides on the porphyrin ring.

In summary, the first evidence is presented for formation of a novel tin-bonded iron(III) porphyrin. The species is prepared by two routes, one of which relies on the facile liberation of an alkyl radical from an alkyliron(III) porphyrin. The tributyltin−iron(III) porphyrin complex has potential as a low-temperature initiator for free radical carbon−carbon coupling reactions important in organic syntheses.

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(16) A sizable dipolar contribution is responsible for the downfield shift of the coordinated tributyltin α-CH_2 signal. On the basis of the $(3 \cos^2 \theta - 1)/r^3$ dependence for assumed dipolar shifts, the upfield-shifted porphyrin phenyl signals would indicate a downfield shift for protons in the axial position. The magnitude of the tributyltin α-CH_2 signal dipolar shift would be two to three times greater than the *o*-phenyl dipolar shift, depending on assumptions about axial ligand conformation.