bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters) and Figures 2-6 (^{1}H NMR spectrum of **16**, three ORTEP plots of **16**, and a diagram from atomic coordinates) (22 pages). Ordering information is given on any current masthead page.

Identification of Intermediates and Products in the Reaction of Porphyrin Iron(III) Alkyl Complexes with Dioxygen

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Unlike most PFe^{III+} (P is a porphyrin dianion) complexes, complexes of the type $PFe^{III}CH_2R$ (R = H or CH_3) are reactive toward dioxygen with the ubiquitous PFe^{III}–O–$Fe^{III}P$ as the only reported product.[1] Here we report on ^{1}H NMR studies of this reaction which focus on the detection of intermediates and the fate of the alkyl group. These results should be viewed in the context of extensive previous studies on model systems for dioxygen activation in biological systems (heme oxygenases) involving reaction of dioxygen with PFe^{II}[2] and on the interaction of peracids and hydroperoxides with PFe^{III}.[3] Through these studies a number of reactive intermediates including the peroxobridge complex, PFe^{III}-O-O-$Fe^{III}P$, and the ferryl complexes, PFe^{IV}=O, (B)P-Fe^{IV}=O (B is an amine), and $(P^\bullet)Fe^{IV}=O^+$ ($P^\bullet$ is a porphyrin radical monoanion), have been detected.

Exposure of a toluene solution of $TTPFe^{III}CH_3$ (TTP is the dianion of tetra(*p*-tolyl)porphyrin) to dioxygen at −80 °C produces the ^{1}H NMR spectrum shown at the top of Figure 1. Three species, unreacted $TTPFe^{III}CH_3$, A, and two intermediates, B and C, are present. The distinctive resonance patterns for B and C are consistent with their formulation as high-spin ($S = {}^5/_2$), five-coordinate iron(III) complexes.[4] The line widths of the pyrrole resonances (B, 1490 Hz; C, 1170 Hz) are consistent with an oxygen donor occupying the fifth coordination site.[5] Intermediate B is quite unstable, even at −80 °C. After standing for 2 h at −80 °C, the ^{1}H NMR spectrum of the sample is converted into that shown in the lower trace of Figure 1. Only C is present.

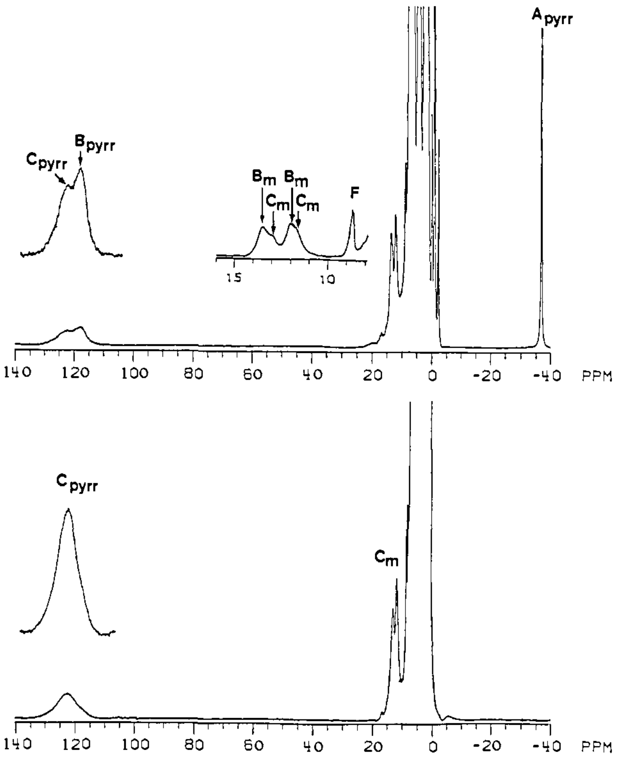

Figure 1. The 360-MHz ^{1}H NMR spectrum of a toluene-d_8 solution of $TTPFe^{III}CH_3$ at −80 °C (a) after the addition of (b) 2 h later. Peaks due to $TTPFe^{III}CH_3$ and the two intermediates are labeled A, B, and C, respectively. Formaldehyde is labeled F, but its intensity is not comparable to other paramagnetic peaks because of spectrometer conditions. The pyrrole resonances are indicated by subscript pyrr, and the meta/phenyl resonances by subscript m.

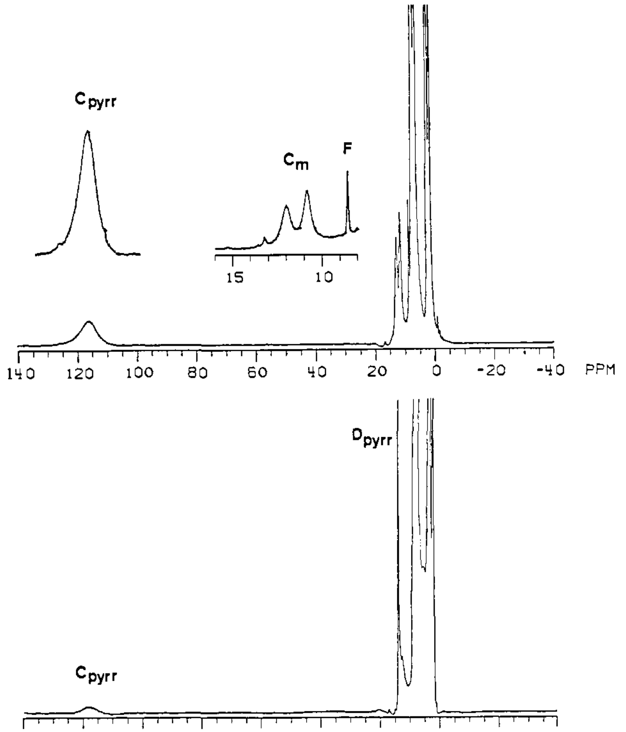

Figure 2. The 360-MHz ^{1}H NMR spectrum of the sample shown in Figure 1: (a) after warming to −70 °C and (b) after warming to 25 °C, storing for 2 h at 25 °C, and then cooling back to −70 °C. Peaks are labeled as in Figure 1 with D indicating $TTPFe^{III}OFe^{III}TTP$.

Intermediate C is also unstable. Figure 2 shows the ^{1}H NMR

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spectrum of C at −70 °C at the top and the sample after warming to 25 °C and then recooling to −70 °C. Most of C has decomposed to form the ultimate product, TTPFe^{III}–O–Fe^{III}TTP, D.[6] Intermediate C has been prepared independently by treating a toluene-d_8 solution of TTPFe^{III}Cl with sodium hydroxide,[5,7] and this material converts to D under the conditions of Figure 2. Thus C is identified as the hydroxy complex TTPFe^{III}OH, which is known to undergo dehydration to give the oxo-bridged product.[5,7]

Examination of the 0–10-ppm region of the ^{1}H NMR spectrum at −70 °C after the formation of C (but before conversion to D) shows the growth of a resonance (F in Figure 1) at 8.6 ppm which is consistent with the formation of formaldehyde. No evidence for the formation of methanol (at 3.0 ppm) is present in the spectrum. More convincing evidence for conversion of the alkyl group into the corresponding aldehyde comes from observations on TTPFe^{III}C$_2$H$_5$. Intermediates analogous to B and C are detected after low-temperature addition of dioxygen. Resonances at 9.14 ppm, q (J = 3 Hz) and 1.40 ppm, d (J = 3 Hz) are indicative of the formation of acetaldehyde. Traces of ethanol 3.30 ppm, q (J = 7 Hz) and 0.93 ppm, t (J = 7 Hz) are present. The ratio of acetaldehyde/ethanol is 96/4. No other organic products are detected.

Related observations have been made with TMPFe^{III}CH$_3$ (TMP is the dianion of tetramesitylporphyrin). Addition of dioxygen to a toluene-d_8 solution of TMPFe^{III}CH$_3$ requires a higher temperature (−50 °C) to produce an intermediate analogous to B (pyrrole, 108 ppm). On standing at −50 °C for 1 h, this intermediate is converted into TMPFe^{III}OH (pyrrole, 104 ppm), an analogue of C which is stable.[5] During this process there is no evidence for the buildup of detectable concentrations of the previously identified intermediates, TMPFe^{III}–O–O–Fe^{III}TMP, TMPFe^{IV}=O, or (TMP$^{\bullet}$)Fe^{IV}=O.[2,3]

Intermediate B is identified as the hydroperoxide anion complex, PFe^{III}–O–O–CH$_2$R. The alternative formulation as the alkoxide complex PFe^{III}–OCH$_2$R is untenable, since such alkoxide complexes are stable throughout the temperature range of our experiments and do not convert into PFe^{III}–OH and PFe^{III}–O–Fe^{III}P.[9]

Our observations indicate that the oxygenation process proceeds via the three steps given in eq 1, 2, and 3. There are limited

$$\mathrm{PFe^{III}{-}CH_2R\ (A) + O_2 \rightarrow PFe^{III}{-}O{-}O{-}CH_2R\ (B)} \quad (1)$$

$$\mathrm{PFe^{III}{-}O{-}O{-}CH_2R\ (B) \rightarrow PFe^{III}{-}OH\ (C) + O{=}CHR} \quad (2)$$

$$\mathrm{2PFe^{III}{-}OH\ (C) \rightarrow PFe^{III}{-}O{-}Fe^{III}P\ (D) + H_2O} \quad (3)$$

precedents for conversion of other metal alkyl complexes into metal hydroperoxide anion complexes (eq 1).[8] If reaction 1 occurs via homolysis of the Fe–C bond, the PFe^{II} product never diffuses far enough to allow for the formation of PFe^{III}–O–O–Fe^{III}P, the known product of the PFe^{II}/O$_2$ reaction under the conditions of our experiments.[2] Again, while the intimate details of reaction 2 are not wholly apparent, homolysis of the O–O bond to form PFe^{IV}O and $^{\bullet}$OCH$_2$R is a likely possibility. However, $^{\bullet}$OCH$_2$R, if formed, must be rapidly oxidized by PFe^{IV}O since very little alcohol, which would result from the reaction of $^{\bullet}$OCH$_2$R with toluene, is produced.

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(9) **Note Added in Proof**: This has been verified by ^{2}H NMR experiments which show distinctly different CD$_2$CD$_3$ resonances for TTPFeOCD$_2$CD$_3$ and TTPFeOOCD$_2$CD$_3$.

Synthesis and Structure of the Iron–Selenium Cubane Cluster [(η^5-C$_5$H$_5$)$_4$Fe$_4$Se$_4$]$^{3+}$: The Fourth Member of the [(η^5-C$_5$H$_5$)$_4$Fe$_4$Se$_4$]^n Series (n = 0 to 4+)

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Transition-metal–chalcogen cubane system is one of the important models of understanding the relationship between electron count and geometrical structure of metal clusters. In contrast to sulfur derivatives,[1,2] selenium derivatives have attracted less attention. Cyclopentadienyl iron–selenium derivatives, [Cp$_4$Fe$_4$Se$_4$]^n (Cp = η^5-C$_5$H$_5$), only a series of organometallic metal–selenium cubane clusters reported so far, show four electrochemically reversible redox waves indicating the existence of five oxidation states, although only three of them, n = 0, 1+, and 2+, have been isolated and structurally characterized.[3,4]

We report the synthesis and crystallographic determination of the fourth member of this oxidation series, [Cp$_4$Fe$_4$Se$_4$]$^{3+}$, the first cubane cluster possessing 17 skeletal electrons, based on high yield synthesis of the neutral and dicationic species.

Roder obtained [Cp$_4$Fe$_4$Se$_4$] (**1**) in poor yield (2.7%) from the reaction of [Cp$_2$Fe$_2$(CO)$_4$] with commercial selenium in refluxing toluene.[3] We found that the reaction of [Cp$_2$Fe$_2$(CO)$_4$] with red selenium Se$_8$[5] ($^3/_8$ molar equiv) in toluene at 60∼70 °C for 2 days leads to the formation of **1** in almost quantitative yield. Dark brown crystals of **1** were isolated in 90% yield after removal of solvent and recrystallization by Soxhlet extraction with CH$_2$Cl$_2$. Alternatively, the reaction of [Cp$_2$Fe$_2$(CO)$_2$(μ-SEt)$_2$][6] with commercial selenium in refluxing toluene for 2 h afforded **1** in 80% yield.

A cyclic voltammogram of **1** in CH$_2$Cl$_2$ containing 0.1 M (n-C$_4$H$_9$)$_4$NBF$_4$ (TBAB) as a supporting electrolyte shows four redox waves as shown in Figure 1a. Complexity of the cathodic waves from +0.7 to +0.2 V versus SCE is possibly due to the adsorption of polycationic cubane clusters on the electrode. The five oxidation states of the [Cp$_4$Fe$_4$Se$_4$]^n system have been reported to be n = 1−, 0, 1+, 2+, and 3+.[3] However, this assignment should be corrected to n = 0, 1+, 2+, 3+, and 4+ since the polarogram of a CH$_2$Cl$_2$ solution of **1** (Figure 1b) shows three anodic waves corresponding to three-step one-electron oxidation and no cathodic wave is observed.[7]

On the basis of this redox behavior of **1**, the bulk electrolysis of **1** was carried out in acetonitrile with 0.1 M NH$_4$PF$_6$ as a supporting electrolyte at +0.60 V versus SCE. After the usual workup, a dication salt, [Cp$_4$Fe$_4$Se$_4$](PF$_6$)$_2$ (**2**),[3] was obtained in 90% yield. The dication salt **2** shows well developed four reversible, one-electron waves in 0.1 M TBAB acetonitrile.

Further oxidation to trication was achieved starting from **2**: Oxidation of **2** in acetonitrile in a manner similar to the synthesis of **2** at +1.0 V versus SCE followed by recrystallization from acetone gave [Cp$_4$Fe$_4$Se$_4$](PF$_6$)$_3$·CH$_3$COCH$_3$ (**3**) as dark brown needles in 83% yield.[8]

The structure of the Cp$_4$Fe$_4$Se$_4$ unit in trication salt [Cp$_4$Fe$_4$Se$_4$](PF$_6$)$_3$·CH$_3$CN (**4**) is shown in Figure 2.[9] Although

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(7) We have recently found that the sulfur analogue, [Cp$_4$Fe$_4$S$_4$]^n also takes five oxidation states assigned to n = 0, 1+, 2+, 3+, and 4+, instead of n = 1−, 0, 1+, 2+, and 3+ as reported previously.[2]

(8) Anal. Calcd for C$_{23}$H$_{26}$F$_{18}$Fe$_4$OP$_3$Se$_4$: C, 21.37; H, 2.03. Found: C, 21.37; H, 2.23.

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