Reaction of Carbon Tetrachloride with 5,10,15,20-Tetraphenyl-porphinatoiron(II) [(TPP)Fe^{II}]: Evidence for the Formation of the Carbene Complex [(TPP)Fe^{II}(CCl$_2$)]

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Summary The reaction of 5,10,15,20-tetraphenylporphinatoiron(II) [(TPP)Fe^{II}] with carbon tetrachloride in the presence of an excess of reducing agent leads to a complex having properties consistent with the carbene, :CCl$_2$, bound to Fe^{II}; this is believed to be the first example of a carbene complex of a metalloporphyrin.

Iron(II) complexes,[1] particularly iron(II) porphyrins[2] and haemoproteins,[3] are known to react with halogenated compounds with carbon–halogen bond cleavage. Involvement of complexes with a metal–carbon bond has been postulated in some of these reactions. Although we reported[4] that the reaction between deutero-porphyrin-iron(II) and CCl$_4$ gives such a complex which is stable in this particular case, we did not discuss the nature of the chloromethyl residue bound to Fe^{II}. Data have also been reported recently supporting the formation of carbene complexes of iron(II) cytochrome P450 on reduction of various polyhalogenated compounds.[5]

We now report the isolation of the product of reaction of 5,10,15,20-tetraphenylporphinatoiron(II) [(TPP)Fe^{II}] with CCl$_4$, under reducing conditions, which has properties corresponding to the carbene complex [(TPP)Fe^{II}(CCl$_2$)].

Addition of deoxygenated CCl$_4$ to a benzene solution of [(TPP)Fe^{II}] results in the disappearance of the bands due to the latter in the visible spectrum and the appearance of new bands due to [(TPP)Fe^{III}Cl] and a new species (I). The new compound (I) [λ_{max} 408 (ϵ 2 × 10^5), 525 (ϵ 15 × 10^3), and 550 (sh) nm in benzene] is also obtained when [(TPP)Fe^{III} Cl] is reduced with an excess of a reducing agent, *e.g.* dithionite (C_6H_6–H_2O or CH_2Cl_2–H_2O, two-phase system), H_2–Pd (H_2O saturated C_6H_6), or iron powder (*NN*-dimethylformamide or CH_2Cl_2–MeOH), in the presence of CCl$_4$; its complete formation requires 1 mol. equiv. of CCl$_4$. A spectrophotometric titration[6] shows that the stoicheiometric reaction performed with the system dithionite–C_6H_6–H_2O involves the liberation of two chloride ions in addition to the chloride ligand of the starting Fe^{III} complex.

In a preparative experiment, a CH_2Cl_2–MeOH (9:1) solution of [(TPP)Fe^{III}Cl] (0·25 mmol) and CCl$_4$ (0·5 mmol) was stirred under argon in the presence of an excess of iron powder for 1 h. Filtration, evaporation of the solvents, washing of a CHCl$_3$ solution of the residue with water, recrystallisation from CHCl$_3$–MeOH, and heating at 100 °C at 10^{-2} mmHg for 10 h gave (I) as a purple-red solid (90% yield) whose elemental analysis (C, H, Cl, Fe, N) agrees with the formula $C_{45}H_{28}Cl_2FeN_4$ of [(TPP)Fe(CCl$_2$)]. The mass spectrum (70 eV, 220 °C) of (I) exhibits the molecular ion at *m/e* 750 (for ^{35}Cl); this peak disappears at higher temperatures with the simultaneous appearance of peaks characteristic of tetrachloroethylene, the dimerisation product of the carbene, $:\mathrm{CCl_2}$.

The preparation of (I) involving an excess of reducing agent, the similarity of its optical spectrum to that of $[(\mathrm{TPP})\mathrm{Fe^{II}(CO)}]$, and its oxidation to the $\mathrm{Fe^{III}}$ state by oxygen (half-life in aerated benzene, 4 h) suggest that it is an $\mathrm{Fe^{II}}$ complex. This is confirmed by its ^{1}H n.m.r. spectrum [δ ($\mathrm{CDCl_3}$, $\mathrm{SiMe_4}$) 7·71 (m, *m*- and *p*-phenyl H), 8·12 (m, *o*-phenyl H), and 8·77 (s, pyrrole H)] which does not display paramagnetic shift or broadening and which is similar to that of $[(\mathrm{TPP})\mathrm{Fe^{II}(pyridine)_2}]$. The ^{13}C n.m.r. spectrum of (I) exhibits, in addition to the signals due to the carbon atoms of the porphyrin ring, δ ($\mathrm{CDCl_3}$, $\mathrm{SiMe_4}$) 146, 141·6, 133·4, 132·3, 127·6, 126·6, and 122 p.p.m., a sharp peak at 224·7 p.p.m. which can actually be observed when (I) is prepared from $^{13}\mathrm{CCl_4}$. The ^{1}H and ^{13}C n.m.r. data are indicative of an axial symmetry and give a chemical shift of the carbon atom derived from $\mathrm{CCl_4}$ which is in the range of those of carbenes bound to transition metals,[7] similar to that of ^{13}CO bound to $\mathrm{Fe^{II}}$ porphyrins or haemoproteins,[8] but very different from that of the ethoxycarbonylmethylene carbon atom (25·7 p.p.m.) inserted into the Ni–N bond of $[(\mathrm{TPP})\mathrm{Ni^{II}}]$.[9] This strongly suggests that the $\mathrm{CCl_2}$ residue is axially bound to the iron atom. Accordingly, complex (I) readily binds one pyridine molecule with a high affinity to give a new complex [formation constant $K = 3500\ \mathrm{l\ mol^{-1}}$ at 20 °C; $\lambda_{\max}$ 423 (ϵ $2{\cdot}4 \times 10^5$), 504 (ϵ $9{\cdot}6 \times 10^3$), and 544 (12×10^3) nm in benzene]. The latter is slowly transformed into the known $[(\mathrm{TPP})\mathrm{Fe^{II}(pyridine)_2}]$[10] only by further addition of a large excess of pyridine.

All our data are in agreement with a pentaco-ordinated $[(\mathrm{TPP})\mathrm{Fe^{II}}]$ complex with a $:\mathrm{CCl_2}$ ligand, which is believed to be the first isolated carbene complex of an iron porphyrin as well as the first dihalogenated carbene complex of a transition metal, and is believed to form as shown in the Scheme.

$$[(\mathrm{TPP})\mathrm{Fe^{II}}] + \mathrm{CCl_4} \rightarrow [(\mathrm{TPP})\mathrm{Fe^{III}Cl} + \cdot\mathrm{CCl_3}] \xrightarrow[-2\mathrm{Cl}^-]{+2e^-} [(\mathrm{TPP})\mathrm{Fe^{II}CCl_2}]$$

However, one cannot completely exclude a hexaco-ordinated carbyne type[11] structure $[(\mathrm{TPP})\mathrm{Fe(Cl)(CCl)}]$ and further investigations, including *X*-ray analysis, are in progress.

Other polyhalogenated compounds such as $\mathrm{CBr_4}$, $\mathrm{CCl_3Br}$, $\mathrm{CCl_3F}$, $\mathrm{CCl_3CN}$, $\mathrm{CCl_3CO_2Et}$, and $\mathrm{CF_2Br_2}$ react similarly with $[(\mathrm{TPP})\mathrm{Fe^{II}}]$.

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