Synthesis of 5,10,15,20-tetra(ruthenocenyl)porphyrin and 5,10,15,20-tetra(ferrocenyl)porphyrin

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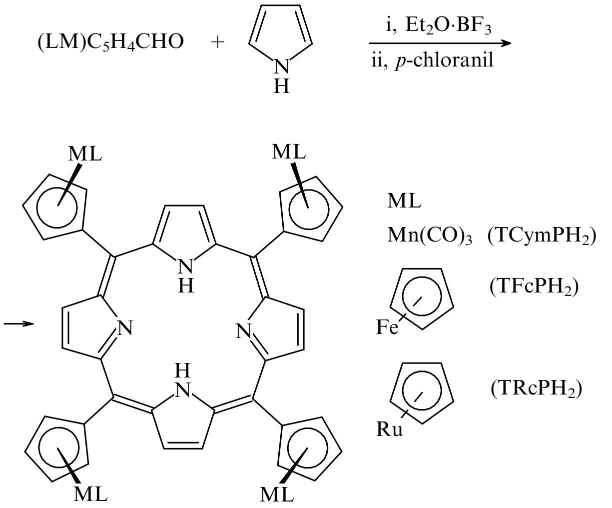
Using the Lindsey method the title compounds were prepared from the corresponding metallocenecarbaldehydes and pyrrole in 56% and 40% yield respectively.

The combination of a porphyrin system and organometallic fragments within the same molecule may be interesting in terms of both catalytic properties and intramolecular charge-transfer.[1–6] However, in most known cases metallocenes are linked to a porphyrin core through some spacers.[1,5,6] One can expect that the presence of a direct bond between the porphyrin and the metallocene would lead to novel approaches in the application of porphyrins. Only three reports on such systems are known. In 1977 a synthesis of *meso*-tetra(ferrocenyl)porphyrin was claimed by Wollmann and Hendrickson.[2] Recently we have reported the preparation of *meso*-tetra(cymantrenyl)porphyrin[3] and its optically active homologue, *meso*-tetrakis[(1*S*)-2-methylcymantrenyl]porphyrin.[4]



We have now extended the synthetic approach, using the Lindsey procedure,[8] to the synthesis of *meso*-porphyrins bearing ruthenocenyl or ferrocenyl groups. The reaction between pyrrole and ruthenocenecarbaldehyde in CH_2Cl_2 in the presence of boron trifluoride etherate (C_4H_5N : RcCHO : BF_3OEt_2 = 1.1 : 1.0 : 0.1) under argon at room temperature for 20 h gave rise to a porphyrinogen that was oxidized without isolation by using *p*-chloranil (0.8 equiv., 3 h). Column chromatography on SiO_2 with benzene–triethylamine (100 : 1) as eluent afforded 54% of a violet-green solid whose spectral characteristics[†] corresponded to those expected for tetra(ruthenocenyl)porphyrin, $TRcPH_2$.

These data for $TRcPH_2$ are basically different from those published[2] for $TFcPH_2$; this seems impossible as ferrocene and ruthenocene are close structural and electronic analogues. The ^1H and ^{13}C NMR spectra of $TRcPH_2$ as well as ones of $TCymPH_2$[3] at the room temperature evidence a high symmetry of these molecules (D_{2h}) due to free rotation around the C–C bond between *meso*-carbon atoms and metallocenyl substituents. The UV-Vis spectrum of this compound is also typical of *meso*-tetraarylporphyrins.[7,8] In contrast, spectra of the compound supposed to be $TFcPH_2$ in ref. 2 are ill-defined, without characteristic features (Figures 1*a*, 2*a*) and difficult to interpret in terms of the structure assumed. The previous authors put forth a hypothesis about the existence of a set of atropoisomers. This led us to synthesize $TFcPH_2$.

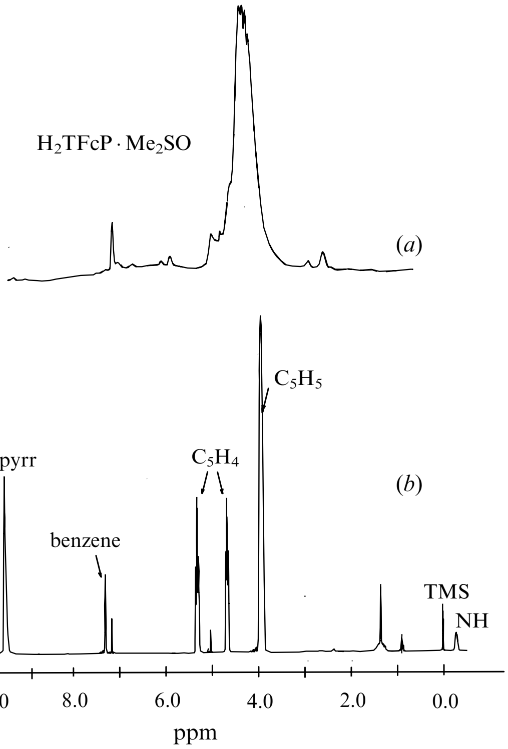


Figure 1 ^1H NMR spectra of $TFcPH_2$ (*a*) corresponding to ref. 2 and (*b*) obtained in this work.

Use of the Lindsey method as described above but with FcCHO instead of RcCHO afforded 40% of a black-green solid which exhibited UV-Vis and NMR spectra[‡] (Figures 1*b*, 2*b*) very close to those of $TRcPH_2$ and corresponded nicely with $TFcPH_2$.

However, boiling FcCHO with pyrrole in AcOH (conditions similar to those in ref. 2) resulted in a product which did have the spectral characteristics given in ref. 2.

[†] ^1H NMR ($CDCl_3$), δ: 9.65 (s, 8H, β-pyrr), 5.71 (m, 8H, α-Cp), 5.08 (m, 8H, β-Cp), 4.35 (s, 20H, CpH), –1.1 (b.s, 2H, NH). ^{13}C NMR ($CDCl_3$): 145.55 (α-pyrr), 130.12 (β-pyrr), 115.54 (*meso*-C), 92.96 (C_i-Cp), 79.57 (α-Cp), 72.31 (CpH), 70.97 (β-Cp). UV-Vis (λ_{max}/nm, CH_2Cl_2, $\varepsilon \times 10^{-4}$): 395 sh (34), 466 (106), 571 (7), 617 (16), 637 (sh), 699 (8); MS-FAB *m*/*z*: 1228 $[M+H^+]$.

[‡] ^1H NMR ($CDCl_3$), δ: 9.62 (s, 8H, β-pyrr), 5.31 (m, 8H, α-Cp), 4.73 (m, 8H, β-Cp), 3.95 (s, 20H, CpH), -0.45 (b.s, 2H, NH); ^{13}C NMR ($CDCl_3$): 145.89 (α-pyrr), 130.62 (β-pyrr), 117.11 (*meso*-C), 88.95 (C_i-Cp), 76.64 (α-Cp), 70.14 (CpH), 68.83 (β-Cp). UV-Vis (λ_{max}/nm, CH_2Cl_2, $\varepsilon \times 10^{-4}$): 435 (134), 480 sh (24), 666 (12.8), 730 (11); MS-FAB *m*/*z*: 1047 $[M+H^+]$.

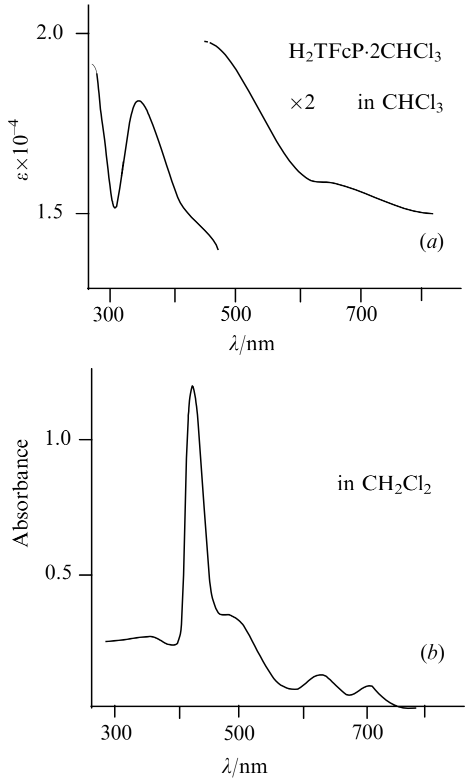


Figure 2 UV-Vis spectra of $TFcPH_2$ (*a*) corresponding to ref. 2 and (*b*) obtained in this work.

To summarize, we have now developed a synthesis of two novel porphyrins which have metallocenyl substituents in *meso*-positions of the porphyrin core; the yields were fair and their structures confirmed by spectroscopic data.

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