^{1}H Nuclear Magnetic Resonance Study and Structure of (Monohydrogen *meso*-Tetraphenylporphyrinato)tricarbonylrhenium(I) †

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Summary (Monohydrogen *meso*-tetraphenylporphyrinato)-tricarbonylrhenium(I) has been prepared; its ^{1}H n.m.r. spectrum in $CDCl_3$ can be interpreted in terms of co-ordination of the rhenium atom by three adjacent pyrrole nitrogen atoms of the porphyrin, with the hydrogen atom bonded to the fourth nitrogen atom of unco-ordinated pyrrole.

Two novel metalloporphyrins of rhenium with meso-porphyrin IX dimethyl ester (MP), namely $H(MP)Re(CO)_3$ and $(MP)[Re(CO)_3]_2$, have been prepared,[1] and structures with the metallo-group out of the porphyrin plane were proposed.[2] These compounds have been suggested as models for an intermediate in metal-ion incorporation into porphyrins.[3] Recently *X*-ray structural studies on μ-(*meso*-tetraphenylporphyrinato)-bis[tricarbonylrhenium(I)], $(TPP)[Re(CO)_3]_2$, showed that each rhenium atom is co-ordinated to three pyrrole nitrogen atoms and that the two opposite pyrrole rings are common to both metal atoms.[4] From its properties, it can be concluded that $(MP)[Re(CO)_3]_2$ has a similar structure to that of $(TPP)[Re(CO)_3]_2$. For $H(MP)Re(CO)_3$ and (monohydrogen *meso*-tetraphenylporphyrinato)tricarbonylrhenium(I), $H(TPP)Re(CO)_3$, rhenium may be co-ordinated to only three adjacent pyrrole nitrogen atoms of the porphyrin and the hydrogen atom may bond with the fourth nitrogen atom of the porphyrin, or it may co-ordinate to four pyrrole nitrogen atoms of the porphyrin and the hydrogen atom may bond still with either one of the nitrogen atoms of the porphyrin, as found for the methylation product of copper corrole.[5] We report the synthesis and ^{1}H n.m.r. study of $H(TPP)Re(CO)_3$, which shows that the first possibility is correct.

(Monohydrogen *meso*-tetraphenylporphyrinato)tricarbonylrhenium(I),$H(TPP)Re(CO)_3$, (I) was prepared by refluxing $Re_2(CO)_{10}$ and *meso*-tetraphenylporphyrin in decalin under argon. The solid (I) obtained was chromatographed on

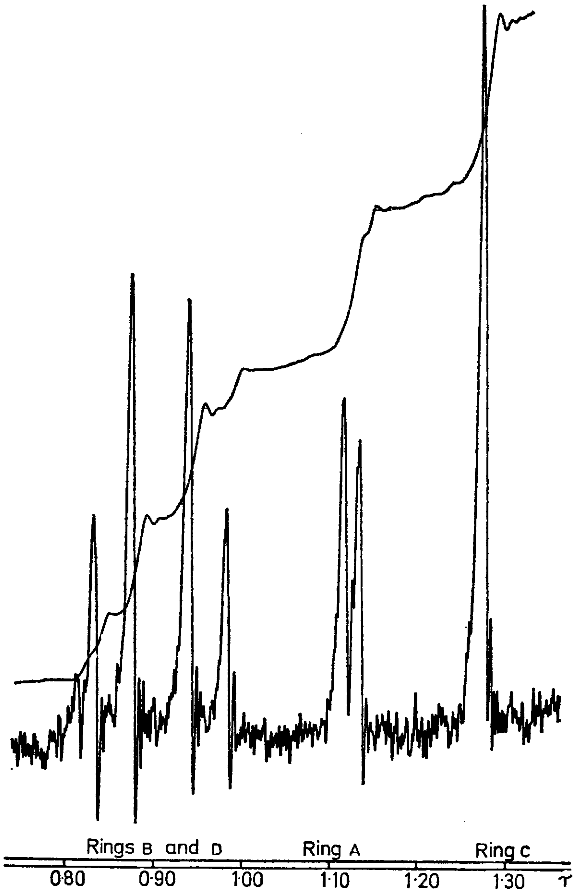

Figure 1. 100 MHz ^{1}H n.m.r. spectrum for the pyrrole protons in compound (I).

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† For previous paper in the series Unusual Metalloporphyrins, see M. Tsutsui and C.-P. Hrung, *Ann. New York Acad. Sci.* in the press.

Sephadex LH-20 with cyclohexane as eluant, and formed air-stable, dark brown crystals (from $CHCl_3$–EtOH); λ_{max} (CH_2Cl_2) 670 (log ϵ 4·920), 473 (5·622), and 402 (6·118) nm; ν_{max} (KBr) 3350 (N–H stretch), and 2010s and 1875s (Re–CO) cm^{-1}; τ ($CDCl_3$) 14·0 (NH), 2·13 (m, *meta*- and *para*-ArH), 1·70 (m, *ortho*-ArH), and 1·28 (s), 1·12 (d, *J* 2 Hz), and 0·89 (J_{AB} 5 Hz, ν_{AB} 12·0 Hz)[6] (all pyrrole-H, relative intensities 2:1:1) (Figure 1). The result can be interpreted if the rhenium atom co-ordinates with three adjacent pyrrole nitrogen atoms (rings B, C, and D) of the porphyrin and the proton binds with the unco-ordinated pyrrole nitrogen atom (ring A) (Figure 2). The β-protons of two pyrrole rings (B and D) are expected to show an AB quartet. The doublet centred at τ 1·12 is due to long-range coupling of β-protons with a nitrogen-bonded proton[7] of the same pyrrole molecule (ring A).‡ The singlet at τ 1·28 can be assigned to the β-protons of pyrrole C.

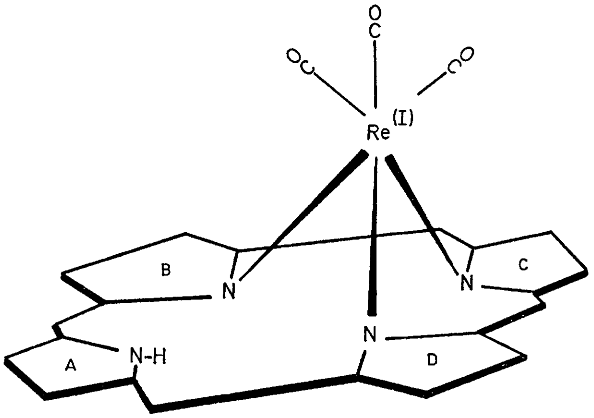

FIGURE 2. Schematic picture of H(TPP)Re(CO)$_3$, (I); the phenyl substituents at the *meso*-positions on the porphin ring have been omitted for clarity.

Thus the ^1H n.m.r. spectrum of (I) can be interpreted in terms of a structure (Figure 2) similar to that of μ-(*meso*-tetraphenylporphyrinato)-bis[tricarbonylrhenium(I)][6], except one of the rhenium atoms is missing and is replaced by a proton which binds only one of the pyrrole nitrogen atoms (ring A).

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‡ The pyrrole nitrogen proton (ring A) in (I) was completely exchangable with deuterium. In this deuteriated sample the doublet centred at τ 1·12 collapsed to a singlet of about twice the peak height but the same area.

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