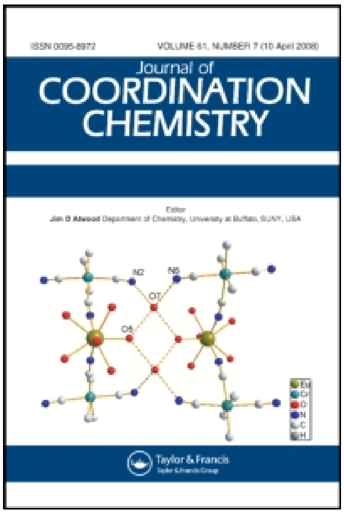

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# UNUSUAL METALLOPORPHYRINS VIII: Synthesis of Ruthenium Mesoporphyrin IX Dimethylester Carbonyl and its Imidazole Derivatives; Observation of a new type of Tautaumerism—Metal Shuttling

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# UNUSUAL METALLOPORPHYRINS VIII

## Synthesis of Ruthenium Mesoporphyrin IX Dimethylester Carbonyl and its Imidazole Derivatives; Observation of a new type of Tautaumerism—Metal Shuttling

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Ruthenium (II) porphyrin complexes have been made with mesoporphyrin IX dimethyl ester and tetraphenylporphine in which one axial position is occupied by a carbonyl group. The other axial position is shown to be either occupied by a loosely bound ligand or entirely empty. The imidazole, 4, 5-dimethylimidazole, and 3, 5-dimethylpyrazole complexes of the mesoporphyrin complex, I, are made. Variable temperature pmr studies on the imidazole and 3,5-dimethylimidazole complexes show the metal nitrogen bond to be moving rapidly between the two imidazole nitrogens at high temperatures.

While the biological significance of the iron porphyrins is well known, many questions about their mode of operation remain unanswered.[1] Much of this undoubtedly involves the protein chain connected to the molecule in the more complex biological systems, but the study of the iron porphyrin, itself, and the atoms bonded directly to it may also be of value.

Studies of iron(II) porphyrins have been carried out, but they are made difficult by the extreme ease with which the iron is oxidized and by the paramagnetism frequently exhibited by iron(II) porphyrins.

While this paramagnetism has proved quite useful in nmr studies on large molecules such as myglobin,[2] paramagnetic broadening will markedly lessen the amount of information to be gained through nmr studies of simpler porphyrin derivatives.

Such considerations led us to synthesize, as a more easily studied analog to an iron(II) porphyrin, a porphyrin derivative of the similarly $d^6$ Ru(II).[3]

## EXPERIMENTAL SECTION

Melting points were determined with a Kofler hot stage microscope and are uncorrected. Ir spectra were run on either a Beckmann IR–12 or Perkin–Elmer Infracord spectrophotometer using sodium chloride cells. Proton magnetic resonance (pmr) spectra were obtained with a Varian HA–100 spectrometer equipped with a variable temperature probe and temperature controller. Temperatures were determined using ethylene glycol and a calibration chart supplied by Varian Associates. Visible spectra were recorded on a Cary-14 spectrophotomer using 10 cm glass cells. All analyses and molecular weight determinations were performed by Schwarzkopf Laboratories.

Reagent grade benzene and tetrahydrofuran (THF) were dried by reflux over lithium aluminium hydride under inert atmosphere for at least 24 hours. The *sym*-tetrachloroethane was distilled from lithium aluminium hydride. 4,5-dimethylimidazole was made by the method of Bredereck and Theilig.[4] Mesoporphyrin IX dimethylester and tetraphenylporphine were made by standard literature methods. All other chemicals were reagent grade and were used without further purification.

*Ruthenium carbonyl mesoporphyrin IX dimethyl ester* (1) To a dry schlenk tube were added 100 mg (0.193 mmole) of mesoporphyrin IX dimethyl ester, 100 mg (0.156 mmole) of ruthenium dodecacarbonyl, and a magnetic stirring bar. The assembly was stoppered, evacuated for half an hour, and refilled with dry argon. Continuing the slow stream of argon, 30 ml of dry benzene was distilled in. A reflux condenser and drying tube were placed on top and, under continued argon pressure, the apparatus was placed in a 100° oil bath so that the oil level was slightly below that of the solvent. Heating and stirring were continued until the visible spectrum of a small sample indicated the reaction was essentially complete. For the quantities given here the period was 24 hours. Larger quantities required longer reaction times and gave lower yields. By using decalin as the solvent, enabling a higher reflux temperature, the reaction time could be cut to as little as one hour.

The solvent was removed under vacuum and the residue dissolved in a small amount of THF. The filtered solution was then evaporated to dryness under a stream of nitrogen. The residue was redissolved in benzene and placed on a column of neutral alumina packed with benzene. Additional benzene eluted a yellow band of unreacted ruthenium carbonyl; methylene chloride eluted the unreacted porphyrin. After collecting these two fractions, the product, **1**, was eluted with a 50/50 methylene chloride/acetone mixture. Some decomposition occured on the column, leaving a black material at the top.

The acetone solution of **1** was evaporated under nitrogen and redissolved in a minimum amount (about a ml) of THF. Several ml of hexane were added and the solution was cooled below 0° for several hours. The suspension was centrifuged, the supernatant decanted, and the microcrystalline residue dried under vacuum at 80° for half an hour.

A yield of 90 mg (74% based on porphyrin) of red, diamagnetic, air-stable **1** was obtained, dec. 290°. It has a typical metalloporphyrin visible spectrum with $\alpha$ and $\beta$ bands at 548 ($\epsilon = 3.4 \times 10^4$) and 518 nm ($\epsilon = 1.53 \times 10^4$) and a Soret band at 393 nm ($\epsilon = 2.85 \times 10^5$) in benzene. The ir spectrum contains a strong absorption at 1940 cm$^{-1}$, confirming the presence of a carbonyl ligand. *Anal.* Calc'd for $RuC_{37}H_{40}O_5N_4$; C, 61.57 H, 5.59; N, 76; Ru, 14.00; molecular weight 721.8. Found: C, 61.28; H, 5.75 N, 7.60; Ru, 13.80; molecular weight (in benzene) 722.

*Ruthenium carbonyl tetraphenylporphine* (**2**) The preparation of this compound was similar to that of **1**. It is also a red, air-stable, diamagnetic solid, dec. 200°. The visible spectrum shows a single absorption at 412 nm and a larger peak at 258 nm. There is a strong carbonyl stretching absorption at 1945 cm$^{-1}$.

*Ruthenium carbonyl mesoporphyrin IX dimethyl ester imidazole* (**3**) Fifty mg (0.070 mmole) of **1**, and 9.5 mg. (0.14 mmole) of imidazole were mixed with benzene and the solution was stirred and heated until the solid dissolved. It was then extracted three times with water, dried with calcium sulfate, filtered, and evaporated to dryness under a stream of nitrogen.

The yield of red crystals was essentially quantitative, mp 203–206°. The visible spectrum contains $\alpha$ and $\beta$ bands at 554 nm ($\epsilon = 8.54 \times 10^3$) and 522 nm ($\epsilon = 6.95 \times 10^3$) and a Soret band at 399 nm ($\epsilon = 1.14 \times 10^5$) in benzene. The ir spectrum in chloroform shows absorptions corresponding to N—H stretching at 3455 cm$^{-1}$, to an ester carbonyl C=O stretch at 1740 cm$^{-1}$, and to the carbonyl ligand C≡O stretch at 1940 cm$^{-1}$. *Anal.* Calcd. for $C_{40}H_{44}O_5N_6Ru$: C, 60.82; H, 5.61; N, 10.64; Ru, 12.80; Molecular weight 789.9. Found: C, 61.03; H, 5.80; N, 10.7; Ru, 12.58; molecular weight (in benzene) 791.

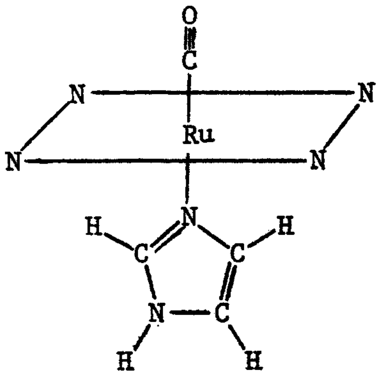
*Ruthenium carbonyl mesoporphyrin IX dimethyl ester* (*4,5-dimethyl imidazole*) (**4**) Fifty mg (0.070 mmole) of **1** were dissolved in several ml of methanol and 7.0 mg (0.073 mmole) of 4,5-dimethylimidazole was added. The mixture was heated and stirred to bring about dissolution, and filtered through a small glass frit. It was then cooled to below 0° for several hours. The suspension was centrifuged, the supernatant decanted, and the residue dried under vacuum at 80° for 30 minutes to give 41 mg (72% yield) of **4**; mp 152–155°. *Anal.* Calc'd for $C_{42}H_{42}O_5N_6Ru$: N, 10.27. Found: N, 10.56.

*Ruthenium carbonyl tetraphenylporphine imidazole* (**5**) This was made by using the same procedure as with **4**, mp 200°. *Anal*: Calc'd for $C_{48}H_{32}N_6ORu$: N, 10.38. Found: N, 10.33.

*Ruthenium carbonyl mesoporphyrin IX dimethyl ester* (*3,5-dimethylpyrazole*) (**6**) This was made using the same procedure as with **4**.

*Ruthenium carbonyl mesoporphyrin IX dimethyl ester pyridine* (**7**) This was not isolated, but was made in the nmr tube by adding a small excess of pyridine to a solution of **1** in benzene.

In solid **1**, the 6th coordination site, trans to the carbonyl group, is apparently occupied by an ester carbonyl. In addition to the two bands at 1725 and 1745 cm$^{-1}$ the ir also shows a stronger one at



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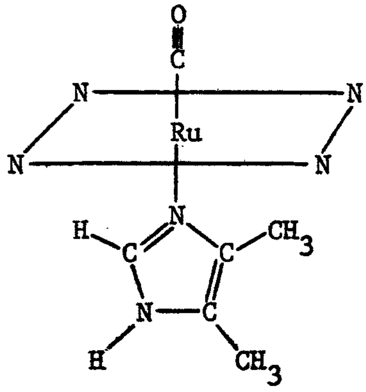

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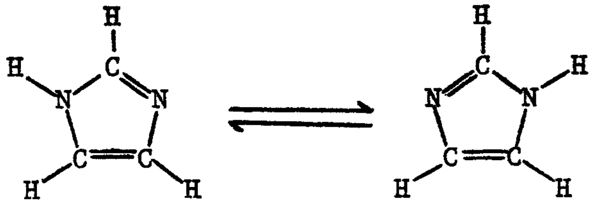

5

$1690^{-1}$, assigned to the coordinated ester. Such a decrease in wave length upon coordination has been observed previously.[5] Both **1** and **2** are only slightly soluble in non-coordinating solvents (hexane, benzene, methylene chloride), but in the presence of small amounts of a ligand (e.g. amines, alcohols), the solubility is increased by several orders of magnitude. The ir spectra of such solutions show only a single ester carbonyl absorption, at 1730 cm$^{-1}$, thus showing the ester carbonyl is no longer coordinated. Similar solubility behavior is also exhibited by the TPP complex, **3**, thus showing that it is not related to the necessity of breaking the bond between metal and ester carbonyl.

The sixth ligand is held very loosely considering that Ru(II) is characteristically "inert" to substitution reactions. This seems to indicate that the five coordinate complex is—at least—a readily accessible transition state. A solution of **1** or **3** in $CHCl_3$ (in which the 0.75% ethanol is presumably coordinated to the ruthenium) forms an adduct with imidazole rapidly, with no change in the carbonyl vibration at 1930 cm$^{-1}$. This imidazole adduct is also rapid in its dissociation upon dissolution in a polar solvent. While recrystallization of the ruthenium porphyrin carbonyl from solution with small amounts of weak ligands present affords intermolecularly coordinated solid with an ester carbonyl band at 1690 cm$^{-1}$, recrystallization from methanol-water apparently leaves a solid with a coordinated methanol or water, as evidenced by the single broad ester carbonyl bond at 1720 cm$^{-1}$ in the ir.

As a possible explanation for why the sixth ligand is either absent or weakly bonded, it was noted that approximate calculation from nmr data indicates the ruthenium atom is 0.5 Å above the plane of the ring (toward the carbonyl).[3] Such positioning would result in steric interaction between any but the smallest ligand and the porphyrin ring. While this should not prevent coordination in the sixth position, it is expected to cause such coordination to be energetically less favorable than would otherwise be the case.

The calculation of the out of plane position of the metal atom is based on the fact that the $\gamma$ proton of the coordinated pyridine in **7** is shifted from the free ligand position by 1.95 ppm. Storm[6] has found the relationship between ring current induced chemical shift ($\Delta$) and the distance, $r$, between that proton and the porphyrin ring current loop to be $\Delta = 66.6/r^2$.

The radius of the porphyrin current loop is known to be 2.2 Å; using this and the nmr results the distance between the center of the porphyrin and the pyridine $\gamma$ proton is calculated to be 5.43 Å. Subtracting the given[6] distance of 3.90 Å between the pyridine nitrogen and the $\gamma$ proton, one gets a distance of 1.53 Å between the nitrogen and the center of the porphyrin ring. A typical Ru-N single bond distance of 2.03 Å[7] would place the ruthenium atom 0.50 Å above the plane of the ring.

The behavior of the imidazole complexes in variable temperature nmr studies has been discussed previously[3] and explained in terms of a rapid "shuttling" of the metal-nitrogen bond between the two imidazole nitrogens.

The room temperature 100 MHz pmr spectrum of **3** in *sym*-tetrachloroethane showed two peaks, with areas corresponding to one proton each, at 9.0 and 9.4$\tau$. As the temperature is raised, they first broaden and then coalesce at about 100° to a singlet with an area corresponding to two protons (Figure 1).

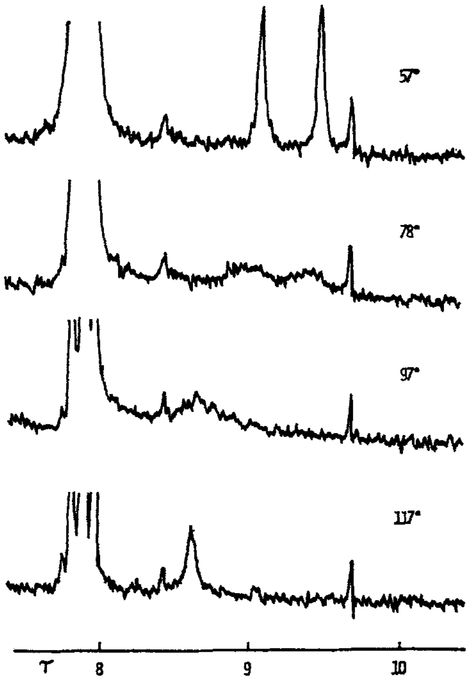

FIGURE 1 PMR spectra (100 MHz) of **3** in *sym*-tetrachlorethane at various temperatures.

The two high field peaks in the spectrum of **3** were assigned to imidazole protons 4 and 5 by comparison with the similarly positioned methyl peaks in the spectrum of IV. The upfield shifts from the free ligand positions are, in both cases, ascribed to the influence of the porphyrin ring current. The room temperature pmr spectrum of **4** contains two sharp singlets whose areas correspond to three protons each, at 10.0 and 11.4$\tau$. These peaks also broaden at higher temperature and, at 117°, they form a sharp singlet at 10.0$\tau$ with an area corresponding to six protons.

Further confirmation of these assignments comes from the benzene solution of **4**. Resonances corresponding to all three types of carbon bonded protons are apparent in its pmr spectrum. The three peaks come at 9.6, 10.2, and 12.0 with areas corresponding to one, three and three protons, respectively. As the temperature is raised, the three peaks are broadened until at 78° they are hardly distinguishable from the base line (Figure 2).

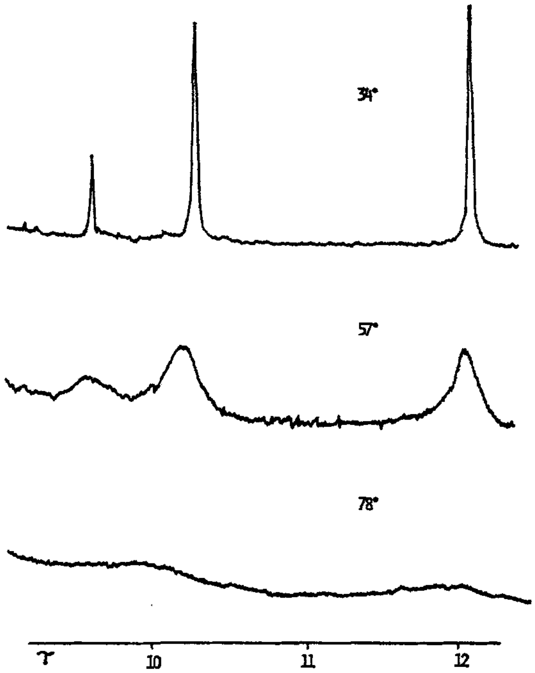

FIGURE 2 PMR spectra (100 MHz) of **4** in benzene at various temperatures.

The reason that the 2-proton does not appear in the spectrum of either **3** or **4** in tetrachloroethane is not clear. A peak corresponding to this proton appears in benzene solution of **4**, as mentioned above, as well as with **3**. Further study shows that, while the 2-proton cannot be seen in many solvents (e.g., chloroform, tetrachloroethane), it can be seen in aromatic solvents (benzene, toluene, mesitylene).

As the temperature is raised in these pmr studies there was noticed both a movement in the peak positions of the imidazole protons and a broadening of the resonances due to the imidazole 2-proton.

These are presumably caused by motion of the imidazole molecule underneath the porphyrin ring through a number of different environments. Averaging over these various environments would cause the broadening of the 2-proton and a change in orientation of the imidazole can explain the changing chemical shifts.

At the temperature limit of mesitylene, however, although a single peak can be seen from the averaging of the imidazole methyl groups in **4**, there is no resonance which can be assigned to the rapidly moving 2-proton.

The possibility of rapid intermolecular ligand exchange was checked by adding an excess of 4,5-dimethyl imidazole to a solution of **4** in benzene. A resonance of 8.0$\tau$ was caused by the methyl groups of the free ligand. Increasing the temperature to 78° caused the methyl resonances of the complexed ligand to be broadened only slightly if at all.

These results raise the question of similar behavior in complexes of other heterocycles containing two nitrogen atoms. The problem of intermolecular exchange, however, prevented similar studies from being carried out with the pyrazole series. Dissolving a sample of the 3,5-dimethylpyrazole complex, **6**, in toluene-$d_9$ and adding excess ligand gave a pmr spectrum with two methyl resonances corresponding to the coordinated ligand at 9.7 and 11.7$\tau$ and a resonance corresponding to the 4 proton at 9.3$\tau$. Despite the presence of considerable excess ligand, as shown by the large free ligand methyl peak at 7.7$\tau$, the coordinated ligand peaks are considerably smaller than would be anticipated for a stoichiometric complex. Though such a complex can be crystallized, it seems to exist in a highly dissociated state while in solution. Consistent with such an equilibrium is the fact that the ligand peaks in the pmr spectrum of the above solution broaden as the temperature is raised and, finally, at 89° cannot be seen at all.

On strictly electrostatic grounds the lesser strength of the coordinate bond in the pyrazole series is reasonable, since a nitrogen atom next to a carbon atom (as in imidazole) would be expected to be a better electron donor than a nitrogen atom adjacent to a more electronegative atom (such as the nitrogen in pyrazole).

Other heterocycle complexes of **1** are being prepared for similar studies. An inert inorganic complex is also being prepared to determine the applicability of the proposed mechanism to nonporphyrin systems.

## ACKNOWLEDGEMENTS

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