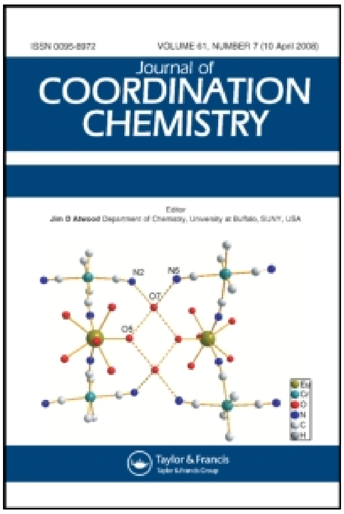

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# UNUSUAL METALLOPORPHYRINS XI. FURTHER STUDIES ON RHENIUM (I) PORPHYRINS

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# UNUSUAL METALLOPORPHYRINS XI. FURTHER STUDIES ON RHENIUM (I) PORPHYRINS

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Experimental details are given for the preparation of two complexes of rhenium with mesoporphyrin IX dimethyl ester, $Re(CO)_3$(H–MPIXDME) and $\mu$-(MPIXDME)$[Re(CO)_3]_2$. The molecular geometry of these complexes is discussed and it is concluded that they do not have simple predictable structures. Three possible structures are discussed for the dirhenium complex. An empirical explanation, similar to the "eighteen electron rule" for metal carbonyls, is given as to why rhenium is in the +1 state. Porphyrin complexes containing a single atom of rhenium and an atom of another metal ($Ag^+$, $Hg^{++}$, or $Pb^{++}$) were detected spectrally but not isolated. Finally the monorhenium complex is compared to the proposed intermediate in metal insertion, in which the metal sits above the porphyrin ring.

## INTRODUCTION

Although a rhenium complex of phthalocyanine had been prepared,[1] our recent communication described the first preparation of a rhenium porphyrin complex.[2] The two compounds prepared were (monohydrogenmesoporphyrin IX dimethyl esterato)tricarbonylrhenium(I), *I*, and $\mu$-[mesoporphyrin IX dimethyl esterato]-bis-[tricarbonylrhenium(I)],*II*.

While the composition of these compounds is clear, the exact structure is not. The current paper describes work which has been done to gain further information on the structure and properties of these unusual metalloporphyrins and to explain their formation.

## EXPERIMENTAL SECTION

### *Materials*

Rhenium and iridium carbonyls[$Re_2(CO)_{10}$ and $Ir_4(CO)_{12}$] were obtained from Alfa Inorganics, and were used without further purification. Mesoporphyrin IX dimethyl ester (MPIXDME) was prepared according to a standard procedure.[3] Decahydronaphthalene (decalin) was distilled at 70° and 30 torr and was kept under argon.

### *Physical Measurements*

Infrared spectra were measured with a Perkin-Elmer 237-B spectrophotometer in chloroform solution. Visible spectra were measured with a Cary 14 spectrophotometer. Mass spectra were obtained on a CEC 21–104 mass spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

*$Re(CO)_3$(H-MPIXDME)* (*I*) A 76.3 mg sample of MPIXDME (0.128 mmol) and 41.9 mg ($6.42 \times 10^{-2}$ mmol) of rhenium carbonyl [$Re_2(CO_{10})$] in 10 ml of decalin were refluxed under argon in a 200° oil bath. A visible spectrum taken after 4 hr showed no change from a spectrum taken after 2 hr and the reaction was stopped. The solution was cooled, filtered, and the solute precipitated by the addition of hexane. The precipitate was then collected and washed with hexane. The crude product was dissolved in dichloromethane, centrifuged to remove undissolved material, evaporated to dryness under a stream of nitrogen, and recrystallized from hot benzene-heptane to give a brown, microcrystalline product, mp 190–192°. *Anal.* Calcd for $ReC_{39}H_{41}N_4O_7$: C, 54.21; H, 4.78; Re, 21.57. Found: C, 54.93; H, 4.89; Re, 22.24. Uv $\lambda_{max}^{C_6H_6}$ 585 ($\epsilon$ $6.2 \times 10^3$), 485($2.0 \times 10^4$), 392 nm ($1.1 \times 10^5$). The ir spectrum included a N–H stretching vibration at 3380 $cm^{-1}$ and carbonyl absorptions at 1900 and 2015 $cm^{-1}$. The mass spectrum showed a parent peak $M^+$ (m/e 862)[4] with a relative intensity of 8.8% compared to the $(M - 3CO)^+$ peak. The relative intensities of the doublet at $(M)^+$ and $(M + 2)^+$ support the presence of one rhenium atom per molecule. The pmr spectrum was that of a complexed porphyrin with the addition of a broad

(half height peak width = 6 cps) peak at $\tau$ 14.9 corresponding to a single proton.

*$\mu$-(MPIXDME)[Re(CO$_3$)]$_2$(II)* The preparation of this compound was similar to that of *I*, except the ratio of reactants was changed. MPIXDME (300 mg, 0.505 mmol) and rhenium carbonyl ($Re_2(CO)_{10}$ (450 mg, 0.690 mmol) were mixed in 10 ml of decalin and refluxed under argon in a 200° oil bath. The visible spectrum of this mixture after two hours was rather similar to that of *I*. Further reaction caused additional spectral change until, after 5 hr, the spectral change stopped. The product, *II*, was purified in a manner similar to *I* and was collected as small dark red needles, mp 250–252°. *Anal.* Calcd for $Re_2C_{42}H_{40}N_4O_{10}$: C, 44.51; H, 3.56; Re, 32.87. Found: C, 44.52; H, 3.99; Re, 32.46. Uv $\lambda_{\max}^{C_6H_6}$ 519, 480 (shoulder), 400 nm. The ir spectrum, both in chloroform and in a KBr pellet, showed strong carbonyl absorptions at 1900 and 2015 $cm^{-1}$. The mass spectrum has a parent peak, $(M)^+$ (m/e 1130)[5] with a relative intensity of 43.8% compared to the $(M - 5CO)^+$ peak. An $(M - 6CO)^+$ peak was also observed with relative intensity of 68.9%. The triplet at $(M)^+$, $(M + 2)^+$, and $(M + 4)^+$ was consistent with two rhenium atoms per molecule, since rhenium exists as two common isotopes, $^{185}Re$ and $^{187}Re$.

*Formation of II from I* A sample of I (2.2 mg, $2.5 \times 10^{-3}$ mmol) was mixed with 0.83 mg ($1.3 \times 10^{-3}$ mmol) of rhenium carbonyl in 5 ml of decalin and refluxed at 200° for 3 hr under argon. The visible spectrum showed the formation of the dirhenium complex, II.

*Attempted Formation of I from II* A sample of the dirhenium complex, II,(2.2 mg, $1.9 \times 10^{-3}$ mmol) and excess MPIXDME (1.4 mg, $2.3 \times 10^{-3}$ mmol) in 5 ml of decalin were refluxed at 200° under argon. Even after 10 hr of reaction no change was observed in the visible spectrum.

*Reaction of Iridium Carbonyl with MPIXDME* A mixture of MPIXDME (30 mg, $5.0 \times 10^{-2}$ mmol) and iridium carbonyl ($Ir_4(CO)_{12}$) (14 mg, $1.3 \times 10^{-2}$ mmol) in 10 ml of decalin was refluxed under argon. The visible spectrum was measured every hour. An absorption appeared shortly at 550 nm and increased in intensity while the free MPIXDME peaks broadened. Before a large amount of the species with the peak at 550 nm had formed, however, the peak began to shrink and finally disappeared. The free MPIXDME spectrum was restored and a shiny, metallic layer formed on the inside of the reaction vessel. Presumably an iridium complex of some sort was formed briefly and then decomposed. A similar reaction carried out in dimethyl formamide showed no evidence of any reaction.

*Reaction of I with $H^+$* Different aqueous buffer solutions were added to samples of I dissolved in acetone. Phthalate buffers were used for *p*H 2–6, phosphate from 6.2–8 and 11–13, and borate from 8.2–10. At higher values of *p*H methanol was also used as a solvent. The addition of acid ($pH \leqslant 1.4$) caused slight demetallation. This was shown by small peaks at 473, 547, and 590 nm, indicative of the $H_2(MPIXDME)^{++}$ dication.[6] The demetallation became serious with the addition of acid at *p*H 0. No other species was observed upon the addition of buffers up to *p*H 13 in methanol and *p*H 11 in acetone.

### *Reaction of Silver Acetate with I*

A sample of *I* (7.5 mg, $8.68 \times 10^{-3}$ mmol) and 1.46 mg silver acetate ($8.72 \times 10^{-3}$ mmol) in 20 ml of acetone containing two drops of triethylamine was refluxed under argon. The color of the reaction mixture changed from light brown to a deep greenish blue after 1 hour of reaction, while in its visible spectrum an additional peak appeared at 650 nm. The reflux was continued for 10 hours without further reaction. The solution was cooled and centrifuged, a silver mirror forming on the centrifuge tube. The supernatant was evaporated under a stream of nitrogen to a gummy material; mp, *ca.* 80°. Further attempts at purification were unsuccessful, partly due to its light-sensitive nature.

### *Reaction of Lead Acetate with I*

A mixture of *I* (45.6 mg, $5.28 \times 10^{-2}$ mmol) and lead acetate (10.0 mg, $2.64 \times 10^{-2}$ mmol) in 20 ml of pyridine was refluxed under argon at 120° for 5 hours. The sharp absorption at 480 nm, characteristic of I, disappeared after 2 hours and was replaced by a new peak at 460 nm. The solution was cooled and centrifuged, but no residue was observed. The pyridine solution was then pumped to dryness without heating. The resulting solid was dissolved in benzene and centrifuged again, a gummy impurity settling out. The clear benzene solution was then pumped to dryness. The crude product, mp 85–90°, could be kept at *ca.* 5° for at least two days without decomposition. However it is decomposed slowly to I at room temperature in air. Further attempts at purification were again unsuccessful.

Both a molecular weight determination and the elemental analysis of the crude product indicated that the lead content was much lower than expected. *Anal.* Calcd for $Re_2C_{78}H_{80}N_8O_{14}Pb$; Pb, 10.71. Found: Pb, 4.94. *Molecular weight.* Calcd: 1931.6 Found: 1330.

### *Reaction of Mercuric Acetate with I*

A mixture of I (5.42 mg, $6.27 \times 10^{-3}$ mmol) and mercuric acetate (1.0 mg, $3.14 \times 10^{-3}$ mmol) in 15 ml of acetone containing 1 drop of triethylamine was refluxed under argon. The reaction was complete after 3 hours with two additional peaks appearing in the visible spectrum at 530 and 570 nm. The solution was cooled, centrifuged, and the solvent removed *in vacuo*. It was then washed with absolute ethanol and the solvent removed again. The crude product was slightly hygroscopic, mp 85–95°. The ir spectrum of its chloroform solution showed no N—H stretching vibration. However, elemental analysis of the crude product showed only half the expected amount of mercury. Calcd for $Re_2C_{78}H_{80}O_{14}Hg$: Hg, 10.41. Found: Hg, 5.66.

## RESULTS AND DISCUSSION

The formation of the two porphyrin complexes is seen to proceed via the following scheme, where *P* represents the porphyrin dianion:

$$(1)\ 1/2Re_2(CO)_{10} + PH_2 \rightarrow Re(PH)(CO)_3$$

$$(2)\ Re(PH)(CO)_3 + 1/2Re_2(CO)_{10} \rightarrow (CO)_3RePRe(CO)_3$$

That these complexes are rather inert is shown by the failure of attempts to prepare the monorhenium complex by reacting the dirhenium complex with free porphyrin. Also significant is the stability of I in acidic and basic media.

This stability and inertness of the rhenium compounds contrasts strongly with the behavior of the stoichiometrically similar pair of Ag(I) porphyrins, $Ag_2P$ and AgHP.[7] Neither the structure nor the bonding of these two silver compounds has been studied, but the similarity of the two visible spectra and the ready decomposition of the complexes, have led to their being considered essentially ionic compounds.[8] As such the metal-ligand interactions would be rather loose and the position of the metal atom(s) is expected to depend substantially on the solvent or the packing of the crystal.

The covalently bonded rhenium complexes, besides being substantially more stable than the Ag(I) (or the alkali metal) porphyrins, should have less structural variation.

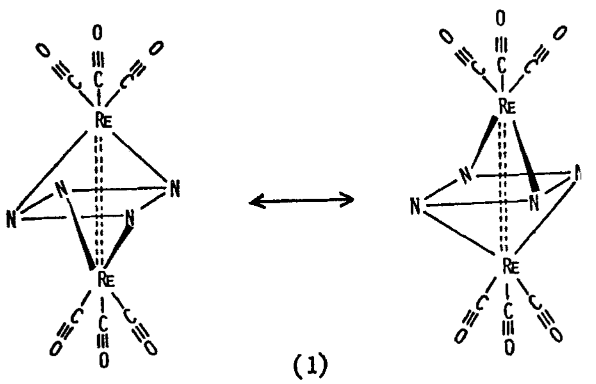
In considering possible structures it should be borne in mind that while the carbon skeleton of a metalloporphyrin can be "ruffled" the inner nitrogen atoms have always been found to be roughly coplanar.[9,10] However, in the diacid of tetrapyridyl porphine the nitrogen atoms are displaced alternately above and below the least squares plane by 0.12–0.13 Å.[6] In addition, it has always been found that the metal atom lies roughly on the symmetry axis of the molecule,[9] and the distance from the center of the porphyrin ring to the pyrrole nitrogens is at least 1.96 Å.[9,10]

In analogy to known metalloporphyrin structures, one would expect the dirhenium complex to contain two metal atoms located on the symmetry axis of the molecule on opposite sides of a planar porphyrin ring. Since the porphyrin ring can be considered to have essentially the same electronic structure as in a typical metalloporphyrin complex, the pyrrole nitrogens will have the same number of electrons available for metal bonding. A structure satisfying these criteria is shown in Figure 1 as structure (1).

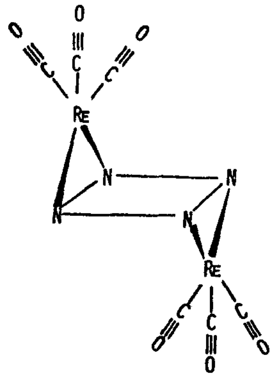
In this structure the eight metal-nitrogen bonds in the dirhenium complex will each have a formal bond number of 1/2. Assuming the covalent radius of Re(I) to be 1.33 Å,[11] the same as that of the isoelectronic Os(II), and correcting the bond length for a bond number of 1/2 by the method of Pauling,[12] one calculates the Re—N bond length as 2.21 Å. If a distance of the pyrrole nitrogen from the center of the ring is taken as 1.96 Å and 2.21 Å from the metal to pyrrole nitrogen, one calculates a Re–Re distance of 2.05 Å. Correcting the calculated Re(I)–Re(I) bond length for a formal order of 2, one gets an expected Re–Re distance of 2.45 Å.

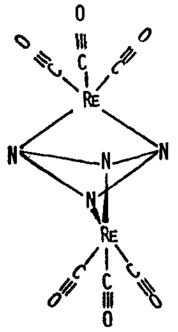
It is conceivable, considering the approximations used, that a rhenium–rhenium bond might be short enough to fit this molecule. However, one must also consider the question of why the carbonyl stretching frequencies are the same for both the mono- and dirhenium complexes. This is unlikely if one compound has a metal-metal bond and the other does not.

Lacking a single crystal X-ray diffraction analysis, a project upon which we are now working, the correctness of structure (1) is at best uncertain. Two other structures can also be formulated which are in agreement with the experimental facts. Structure (2) is unique in that, as mentioned above, the nitrogen atoms of metalloporphyrins have always been found to be roughly coplanar.[9, 10] Such a "folded" structure has been found, but only in the protonated porphyrin dication.[6] Whether structure (1) or (2) is adopted depends on the relative energies of folding the porphyrin ring versus forming a shortened metal–metal bond. A minimum distortion of the porphyrin ring would require a metal–metal bond. However some factor such as van der Waal's repulsion between the metal atoms and their two non-bonded nitrogens, or lack of orbitals suitable for metal–metal bonding, might cause the ring to fold enough to avoid such interaction. Assymetric structures (3) are also consistent with our observations, but have little else to recommend them.



(1)





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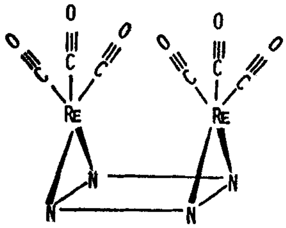

(3)

FIGURE 1 Possible Structures of $\mu$-(mesoporphyrin IX dimethyl esterato]-bis-[tricarbonylrhenium (I)].

A similar set of structures can be proposed for the monorhenium complex, *I*. The problem of choosing among them is equally difficult. However the similarity in the ir spectra of the mono- and dirhenium complexes is probably indicative of similar structures.

It was hoped that possible protonation and/or deprotonation of the porphyrin ring in I, and the attendant spectral changes, would assist in the structure elucidation. Unfortunately no inferences can be made, except on the stability of the complex, from the observed negative results.

The reaction of I to form the dirhenium complex, II, suggested the possibility of making a series of complexes in which the porphyrin ring is bound to both a rhenium atom and an atom of another metal. Although this could not be done with all metals, *I* did react further with several mono- and divalent cations of heavy metals ($Ag^+$, $Hg^{++}$ and $Pb^{++}$) in a basic solvent. Evidence for these reactions came from changes in the visible spectra of the solutions (Table I).

It is presumed that monovalent cations replace the remaining pyrrole proton of *I*, forming a 1:1 complex. Divalent cations are thought to similarly replace a pyrrole proton from each of two molecules of *I*, forming a complex with the heavy metal situated between two porphyrin rings.

TABLE I

Visible absorption maxima for [Re(CO)$_3$ (H–MPIXDME)] and several reaction products

| Compound | λ max |
|---|---|
| I | 400 480, 580 nm |
| Product with silver acetate | 398 480, 560, 580 nm |
| Product with mercury (II) acetate | 398 480, 530, 570, 580 nm |
| Product with lead (II) acetate | 398 460, 580 nm |

The metal-nitrogen bonds thus formed are weak and the products could not be purified due to decomposition in air. Partial decomposition is also shown by the molecular weight and analytical results.

Another question is why rhenium, for which the +1 state is of relatively little importance,[13] uses this oxidation state in forming porphyrin complexes. This is best discussed by comparison with metalloporphyrins from an adjacent area of the periodic table—gold and the platinum metals. Table I shows that in porphyrin complexes formed from these metals the six coordinate compounds have 18 electrons in their valence shells, while the four and five coordinate compounds have 16 valence electrons. This empirical correlation is similar to the "eighteen electron rule" for metal carbonyls[14] and can be similarly rationalized in terms of molecular orbital splittings. The single known exception is a paramagnetic Rh(IV) complex in which one of the axial ligands is a sigma bonded phenyl group.[15]

The only rhenium (and technetium) complex consistent with this "rule" and having the metal in a positive oxidation state would be a five or six coordinate complex in the +1 state. Several structures can be conceived which are consistent with this, among them (1), (2), and (3). Also consistent with this "rule" would be the existence of four coordinate +1 complexes for rhodium and iridium in addition to the six coordinate +3 compounds already prepared.[17] An attempt to make such a compound using iridium carbonyl (instead of the carbonyl halide previously employed)[17] was unsuccessful.

TABLE II

Number of valence electrons in porphyrin complexes of gold and the platinum metals

| Complex[a] | Oxidation State | Coordination Number | Valence Electrons | Reference |
|---|---|---|---|---|
| Ru*PLL′* | 2 | 6 | 18 | 16 |
| Rh*PLX* | 3 | 6 | 18 | 17 |
| Ir*PLX* | 3 | 6 | 18 | 17 |
| Pd*P* | 2 | 4 | 16 | 18 |
| Pt*P* | 2 | 4 | 16 | 18 |
| (Au*P*)+ | 3 | 4 | 16 | 19 |

[a] P is a porphyrin dianion, *L* and *L′* are neutral ligands, and *X* is an anionic ligand.

Also worthy of note is the similarity between these complexes and two species proposed as intermediates in porphyrin insertion.[20, 21] It does not seem likely that either could ever be isolated. Hence the study of these more stable analogs may be useful in determining possible properties of such intermediates.

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