NEW TRENDS IN THE CHEMISTRY OF ORGANOMETALLOPORPHRINS

Minoru Tsutsui
Department of Chemistry, Texas A & M University, College Station, Texas 77843

Abstract - The evolution and the current trends in a new area of chemistry of organometalloporphyrins, in metalloporphyrin chemistry are reviewed. Synthesis and properties of out of plane, di-nuclear, and "Skewered" metalloporphyrins are described. The new chemistry of metalloporphyrins was initiated by the application of Cr(OC)\textsubscript{6}, metal carbonyl in general, for insertion of Cr ion (metal ions) into porphyrins.

Organometalloporphyrins in general are defined as synthetic metalloporphyrin complexes containing at least one direct metal-carbonyl bond. However, the coenzyme of Vitamin B\textsubscript{12} (Figure 1) containing an adenosyl group linked to cobalt by a direct cobalt-carbon \textsigma-bond is the first example of a naturally occurring organometallocorrin complex (similar to organometalloporphyrins in molecular structure) and the first-known stable organocobalt derivative. The determination of the structure of the vitamin B\textsubscript{12} coenzyme by x-ray crystallography, prompted several studies of the synthesis and properties of cobalt-alkyl compounds. Johnson and his co-workers extended their studies to the porphyrin series by reaction of pyridinobromocobalt(III) aetio-porphyrin-I with a variety of alkyl- and aryl-magnesium halides in anhydrous 1,2-dimethoxyethane (DME) to give the corresponding alkyl- and aryl-cobalt(III) derivatives. Ethyl and p-poly-iron (III) derivatives of aetio-porphyrin-I were also prepared by a similar method. The first-row transition metal derivatives of organometalloporphyrins were thus synthesized for the first time. In an alternative synthesis, Johnson and his co-workers were also able to prepare the identical alkyl cobalt(III)aetio-porphyrin-I complexes as that mentioned above, by reduction of cobalt(II)aetio-porphyrin-I with 1% sodium amalgam in DME to form cobalt(I) species, which then react with alkyl halides to give the final products. This method was also used for the preparation of hydroxyalkyl-cobalt(III)aetio-porphyrin-I complexes. Both the cobalt(III) and the iron(III) organometalloporphyrins are sensitive to light, especially in solution, and decompose by homolytic fission of the metal-carbon bond.

The use of metal carbonyls for the insertion of metal ions into porphyrins was first introduced by Tsutsui and his co-workers \textsuperscript{10,11} in 1966 (Figure 2). This method is probably one of the most important developments in porphyrin chemistry within the last two decades. In addition to a number of previously reported metalloporphyrins, the reaction of metal carbonyls and metal carbonyl halides \textsuperscript{12,13} with neutral porphyrins has led to the synthesis of new metalloporphyrin complexes of chromium, molybdenum, technetium, ruthenium, rhodium, rhenium and iridium. Except for the chromium and molybdenum complexes, carbonyl groups...
are retained by the metals in the new metalloporphyrin complexes.

By reaction of dirhenium decacarbonyl, Re₂(CO)₁₀, or ditechnetium decacarbonyl, Tc₂(CO)₁₀, with mesoporphyrin IX dimethylester, H₂MPIXDE, in refluxing decalin under argon, Tsutsui and his co-workers have successfully prepared two unusual rhenium organometalloporphyrins, (H-MP)Re(CO)₃, I, and MP[Re(CO)₃]₂, II, a pair of technetium organometalloporphyrins, (H-MP)₃Tc(CO)₃, III, and MP[Tc(CO)₃]₂, IV, and a mixed rhenium technetium organometalloporphyrin, (OC)₅ReMPTc(CO)₃, V. A single crystal X-ray diffraction analysis of μ-[Me₆C₆-tetraphenylporphinato]bistricarbonylrhenium(I), TPP[Re(CO)₃]₂, VI, (Figure 3), has shown that each rhenium ion is bonded to three nitrogen atoms and that two rhenium atoms are bonded to one porphyrin on opposite sides of the plane of the porphyrin molecule. The metal ions in these complexes, I–VI, sit out of the plane of the porphyrin molecule. The monorhenium and monotechnetium complexes, I and III, where the porphyrin moiety acts as a tridentate ligand, resemble Fleischer's proposed "sitting-atop complex" and are good models for the intermediates in the insertion of a metal ion into porphyrin. The dirhenium, ditechnetium, and mixed rhenium-technetium organometalloporphyrin complexes, II, IV, and VI, where the porphyrin moiety acts as a hexadentate ligand, are examples of the first isolated stable homo- and hetero-dinuclear organometalloporphyrin complexes. The monorhenium porphyrin complex, I, reacts with Re₂(CO)₁₀ or Tc₂(CO)₁₀, in refluxing decalin to form the dirhenium porphyrin complex, II, and the mixed rhenium technetium porphyrin complex, III, respectively. Replacement of the pyrrolic proton (N₃H) of the monorhenium porphyrin complex by other metal ions such as Ag⁺, Hg²⁺, and Pb⁰, has resulted in unstable complexes. The monotechnetium porphyrin complex, III, (Figure 4), behaves in a different manner by disproportionateing to form a ditechnetium porphyrin complex, IV, and the free porphyrin, H₂MPIXDE, by heating in refluxing decalin. This unusual coordination phenomenon has never been reported. Such a reaction was not observed on heating monorhenium porphyrin complex, I, in refluxing decalin. It seems that both the rhenium and technetium dimetalloporphyrin complexes are thermodynamically more stable than the monometalloporphyrin complexes, because a reverse reaction of $\text{M}[\text{M(CO)}₃]_{3}^{2}$ to (H-MP)-M(CO)₃,
(M=Re or Tc), could not be detected between NP[M(CO)₃]₂ and H₂UIX₃n refluxing decalin for either the rhenium or technetium dimetalloporphyrin complexes.

Temperature-dependent ¹H nmr spectral changes for HTPPr(CO)₃ and HMPPr(CO)₃ dissolved in 1,1,2,2-tetrachloroethane showed fluxional behavior of Re(CO)₃ group. This phenomenon is best explained by the intramolecular rearrangement of the metal carbonyl group among the four ring nitrogens of porphin and also movement of the N=H; it can also be regarded as an intramolecular substitution at rhenium or technetium, (Figure 4).³⁵

We have prepared a new salt type complex of porphyrins, monocation octaethylporphyrin tri-μ-halogeno-hexacarbonyldirhenate(I) from the reaction of Re(CO)Cl and H₂OEP in a 2:1 mole ratio in decalin. The structure of the complex was elucidated by the x-ray diffraction analysis method, (Figure 5).³⁶

[Re(CO)₃]₃TPP has been oxidized by SbCl₅ in dichloromethane to yield [Re(CO)₃Cl]₃TPP • 2SbCl₅ and [Re(CO)₃][Re(CO)₃Cl] • SbCl₅. An x-ray determination of the structure of these complexes provides definite evidence for a "skewered complex", that is a metalloporphyrin in which a metal-metal bond exists through the "hole" of the macrocycle, (Figure 6).³⁷

Two different methods were employed by Fleischer and his co-workers in preparing the rhodium and iridium porphyrin complexes.²⁰,²⁴ In one, the freshly prepared metal carbonyl halides, [Rh(CO)₃Cl]₂ and [Ir(CO)₃Cl], were allowed to react with the porphyrins in glacial acetic acid solution to form the respective metalloporphyrins, (Figure 7). In the second method,
the cyclooctene complexes of rhodium and iridium were found to be reactive intermediates useful in the metalloporphyrin formation, (Figure 6). In both methods, incorporation of rhodium into the porphyrin was more readily achieved than was that of iridium. It is of interest that in the metalloporphyrins prepared by these methods, the iridium porphyrins retain the carbon monoxide ligand while rhodium and other metals do not. The carbon monoxide is very tightly bound to the iridium porphyrin moiety; heating, pumping, boiling in pyridine, or reprecipitating from concentrated sulfuric acid solution does not remove the carbonyl group from the complex.24

By the reaction of [Rh(CO)Cl] with meso-tetraphenylporphyrine-H, TPP, in refluxing benzene, two stable organometalloporphyrin derivatives of rhodium, Rh CO(TPP) Cl and (o-phenyl)Rh(TPP) Cl, were separated by chromatography on an alumina column by Fleischer and his co-workers.21,26

Yoshida and his co-workers were able to prepare two novel dinuclear rhodium(I) organometalloporphyrin complexes, [Rh(CO)Cl2]2, VII and VIII, by modifying Fleischer's reaction conditions for the preparation of Rh CO(TPP) Cl and (o-phenyl)Rh(TPP) Cl in refluxing benzene. Octaethylporphyrin, OEPH, or (N-methyl) octaethylporphyrin reacts with [Rh(CO)Cl] in benzene solution at room temperature under nitrogen atmosphere to produce VII and VIII. From the spectral data and experimentally determined molecular weight, VII was formulated as an acid, H [OEP • Rh2(CO)Cl] Cl, which contains a Rh-Cl-Rh bridge. The proton nmr and infrared spectral data indicate that the [Rh(CO)Cl]2 moiety is maintained and the N-H and N-CH2 bonds exist in VII. Since the Rh-Rh distance in [Rh(CO)Cl]2 has been reported to be 3.12 Å, and the distance between the two adjacent nitrogen atoms of planar porphyrin is about 2.9 Å, it was assumed that the two Rh atoms of the [Rh(CO)Cl]2 moiety are bonded to the two adjacent nitrogen atoms of the porphyrinato core of VIII. As
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[Chemical reaction and diagram]

\[ \text{Ir}^3(\text{cycl}_2\text{Cl})_2 \rightarrow \text{ETHANOL} \]

\[ [\text{Ir}^1(\text{cycl}_2\text{COCl})] \rightarrow \text{PH}_2\text{ESTER} \]

\[ \text{CO} \]

\[ \text{Ir}^3 \]

\[ \text{CO} \]

\[ \text{Ir}^3 \]

\[ \text{CYCLOOCTENE} \]

\[ \text{HCl} \]

\[ \text{py} \]

\[ \text{HCl} \]

\[ \text{NaOH} \]

\[ \text{HCl} \]

\[ \text{CO} \]

\[ \text{Ir}^3 \]

\[ \text{Cl} \]

\[ \text{+ Ru}_3(\text{CO})_{12} \]

\[ \text{(TPPH}_2\text{)} \]

\[ \text{BENZENE} \]

\[ \text{IMIDAZOLE} \]

\[ \text{IMIDAZOLE} \]

\[ \text{NO} \]

\[ \text{2NO} \]

FIGURE 8

FIGURE 9
shown in Figure 9. Upon exposure to air, \( \text{VII} \) was slowly oxidized to form a rhodium(III) chloro complex of octaethylporphyrin, \( \text{Rh}^{\text{III}} \text{Cl(OEP)} \cdot 2\text{H}_2\text{O} \), which can further react with alkyl lithium to give an alkyl-rhodium complex, another example of rhodium organometalloporphyrin complex. However, \( \text{VII} \) behaves in a different manner to give the identical alkyl-rhodium complex either by gentle heating in chloroform or chromatography on silica gel (Figure 9). This phenomenon of alkyl migration from a nitrogen atom to a metal ion is reported for the first time. The alkyl migration may proceed concerted with oxidation of rhodium(I) to rhodium(III). The \( \text{N—CH}_3 \) bond fission seems to be facilitated by the aid of a low-valent rhodium ion. The reaction of \( \text{(N-ethyl)octaethylporphyrin with} [\text{Rh(CO)}_\text{Cl}]_\text{2} \) yields a rhodium(I) complex similar to \( \text{VII} \), which is also easily oxidized to \( \text{CH}_3\text{H}^+ \text{Rh(OEP)} \). The mechanism of metal oxidation and alkyl migration is still unknown.

Both ruthenium carbonyl, \( \text{Ru}_3(\text{CO})_\text{12} \), and ruthenium carbonyl halide, \([\text{Ru(CO)}\text{Cl}]_\text{2} \), react with tetraphenylporphyrin to give the identical product, monocarbonyl-ruthenium(II)"tetraphenyl porphine" \( \text{TPPRuCO} \). It was found that \( \text{IX} \) crystallizes with a molecule of either alcohol or water and that these weakly bound molecules are "trans" to the carbonyl group. Recently, a single crystal x-ray diffraction analysis confirmed this structure. Imidazole and similar organic bases complex immediately at room temperature with TPPRuCO upon mixing in benzene. However, as expected for a low spin d^5 system, substitution reactions of the monocarbonyl-ruthenium(II) complex take place slowly and under severe conditions to replace the carbonyl group. Irradiation of degassed benzene or pyridine solutions of monocarbonyl ruthenium(II) meso-tetra(p-sulfonatophenyl)porphinato-cobalt(III), \( \text{Co}^{\text{III}}\text{TPPS} \), and sodium borohydride and found it to be very effective catalyst for the reduction of the substrate of nitrogenase. For example, acetylene was reduced catalytically in this system to ethylene and ethane. A possible mechanism for this catalytic system was proposed to include cobalt-acetylene and cobalt-ethylene metalloporphyrin \( \pi \)-complexes as intermediates (Figure 10). For the induced oxidation of cobalt(II) mesoporphyrin \( \text{M(octaethyl porphyrin)Co}^{\text{III}} \) dimethyl ester, 

Since the successful isolation and purification of nitrogenase, the enzyme system that fixes molecular nitrogen to ammonia in living organisms, many studies have been made to find a nitrogenase model. Fleicher and co-workers created a model system consisting of the water soluble mono-tetra(p-sulfonatophenyl)porphinato-cobalt(III), \( \text{Co}^{\text{III}}\text{TPPS} \), and sodium borohydride and found it to be very effective catalyst for the reduction of the substrate of nitrogenase. For example, acetylene was reduced catalytically in this system to ethylene and ethane. A possible mechanism for this catalytic system was proposed to include cobalt-acetylene and cobalt-ethylene metalloporphyrin \( \pi \)-complexes as intermediates (Figure 10). For the induced oxidation of cobalt(II) mesoporphyrin \( \text{M(octaethyl porphyrin)Co}^{\text{III}} \) dimethyl ester,
solution of toluene. The paramagnetic low-spin d^7 complex of Co^{II}TPP has a single unpaired electron in the dz^2 orbital for bonding with carbon monoxide, which provides an opportunity for the examination by esr of spin delocalization to carbon monoxide.

Similarly, the reversible binding of carbon monoxide to iron(II) protoporphyrin in piperidine was identified by its esr spectrum in frozen solution.

The Ï—interaction in carbon monoxide to metalloporphyrin adducts and the proposed olefin-metal Ï—complex intermediates for induced oxidation of cobalt(II) porphyrin by unsaturated hydrocarbon and the catalytic reduction of acetylene in CoTPPS and NaBH_4 model system has brought new examples of formation of organometalloporphyrins.

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REFERENCES
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