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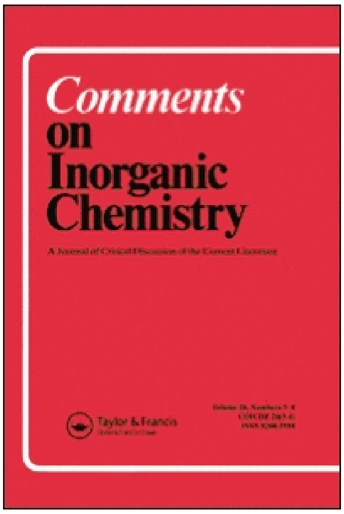

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Metal-Metal Bonds in Metalloporphyrins

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Metal–Metal Bonds in Metalloporphyrins

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The chemistry of metal–metal bonded metalloporphyrins has undergone significant development during the last decade. The synthesis, chemical reactivity, physical properties and electrochemistry of metal–metal bonded metalloporphyrins containing both σ- and donor–acceptor bonds are presented. These new classes of metalloporphyrins are important in biological processes, in synthetic organometallic chemistry, and in the preparation of new materials.

Key Words: *homo and heterobinuclear porphyrins, σ-bonded heteronuclear metalloporphyrins, carbenoid-bonded heteronuclear metalloporphyrins, electrochemical properties*

Three classes of metalloporphyrins with metal–metal bonds have been described in the literature. These are: (i) homo- and heterobinuclear porphyrins of the type (P)MM(P)* or (P)MM′(P); (ii)

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*Abbreviations: P = unspecified Porphyrin, OEP = Octaethylporphyrin; TPP = Tetraphenylporphyrin; TmTP: Tetra-m-tolylporphyrin; TpTP = Tetra-p-tolylporphyrin (see Part 4).

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σ-bonded heteronuclear metalloporphyrin complexes of the type (P)MM'(L) or $[(P)In]_2M'(L)$; (iii) carbenoid-bonded heteronuclear metalloporphyrins of the type (P)MM'(L), or (P)Sn $(Mn(CO)_4HgMn(CO)_5)$ and $(P)Sn(Co(CO)_4)$. Some aspects of the reactivity for these series of complexes have been recently discussed in two reviews.[2,3]

Another group of metal–metal bonded metalloporphyrin complexes are those consisting of conducting polymeric porphyrin units. The properties of those type complexes have been covered in two reviews[4,5] and are not discussed in the present article.

I. DIMERS OF THE TYPE (P)MM(P) OR (P)MM'(P)

This class of compounds includes homobinuclear porphyrins of the type (P)MM(P), where P is one of several different porphyrin rings and M = Rh^{II},[6–11] Ir^{II},[12] Ru^{II},[13] Os^{II} [6] or Mo^{II} [6,14] and heterobinuclear porphyrins of the type (P)MM'(P). These complexes contain either single, double or quadruple metal–metal bonds.

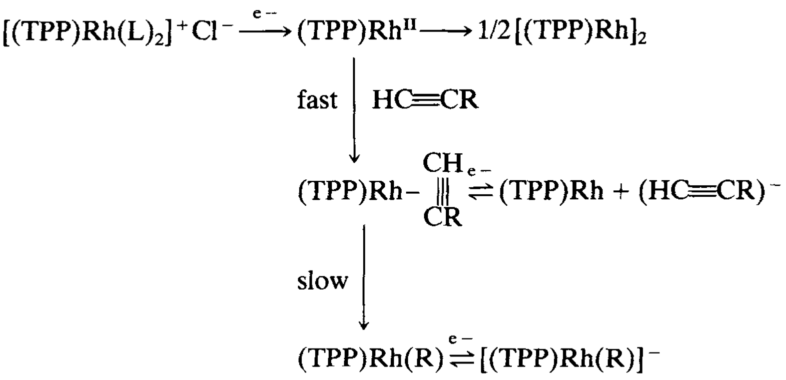
1.A. Single Bonded Homodimers

Di(porphinato)rhodium(II)[6–11] was the first reported metalloporphyrin dimer which contained one single metal–metal bond. Oxidative cleavage (Eq. (1)) or thermal homolytic cleavage (Eq. (2)) of (OEP)RhH will produce $[(OEP)Rh]_2$. The formation of this dimer is consistent with the enhanced covalent-bond-forming properties of second row transition metals. Indeed, low spin cobalt(II) porphyrins are always monomeric species while the only known Rh^{II} porphyrins are dimeric. $[(OEP)Rh]_2$ and its TpTP analog have also been prepared by photolysis of the hydride derivatives.[6,7]

$$2(OEP)RhH \xrightarrow{1/2\ O_2} [(OEP)Rh]_2 + H_2O \qquad (1)$$

$$2(OEP)RhH \xrightarrow{\Delta} [(OEP)Rh]_2 + H_2 \qquad (2)$$

Electrochemical reduction of some Rh^{III} porphyrins can lead to the Rh^{II} dimers.[15,16] For example, the reduction of $[(TPP)Rh(L)_2]^+Cl^-$ where L = dimethylamine generates a highly reactive Rh^{II} species which dimerizes to generate $[(TPP)Rh]_2$ in PhCN, THF, and pyridine. The electrogenerated (TPP)Rh species can



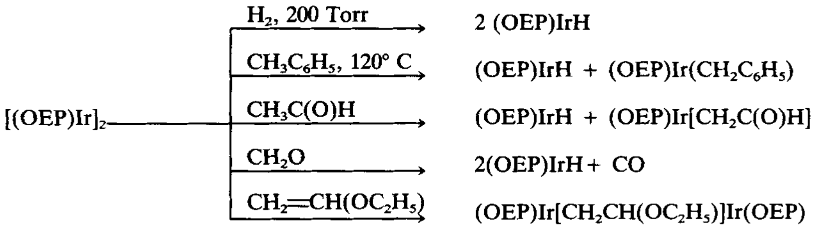
SCHEME I

react with acetylenic or ethylenic derivatives via a π complex as shown in Scheme I where R = n-C_3H_7, n-C_4H_9, n-C_5H_{11} or n-C_6H_{13}. The overall reaction of (TPP)Rh and HC≡CR involves a cleavage of the carbon–carbon bond adjacent to the double or triple bond functionality.

The reactivity of electrogenerated $(TPP)Rh^{II}$ towards RX[15,17] is similar to, but not identical with, that observed for $[(OEP)Rh]_2$.[9,10] For example, the reaction of $[(OEP)Rh]_2$ with RX results in formation of both (OEP)Rh(R) and (OEP)RhX. In contrast, (TPP)RhX is not formed during electrochemical generation of (TPP)Rh(R) from $(TPP)Rh^{II}$ and RX when RX is CH_3CH_2I or $C_6H_5CH_2Br$.

The difference in reaction products between reactions involving (TPP)Rh and (OEP)Rh may be due to the two different methods of generating the monomeric rhodium(II) porphyrin or, alternatively, to the different types of alkyl halides investigated. Moreover, the reaction of $[(OEP)Rh]_2$ with HC≡CR, where R is H or C_6H_5, results in formation of (OEP)Rh(CH=CR)Rh(OEP).[7,8] A binuclear bridge Rh^{III} complex $(OEP)Rh[CH_2CH(C_6H_5)]Rh(OEP)$[18] is also reported to be generated from $[(OEP)Rh]_2$ and $CH_2{=}CHC_6H_5$. In contrast, the reaction of $[(OEP)Rh]_2$ with $CH_2{=}CHCH_2R$, where R is C_6H_5, CN, or n-C_3H_7, produces $(OEP)Rh(CH_2CH{=}CHR)$.[9,10]

In general, rhodium macrocycles form metal–carbon bonds by either a two-electron S_N2-like mechanism[19,20] or by a radical one-electron process.[19,21,22] Kinetic studies involving the reaction of



SCHEME II

$[(P)Rh]_2$ and alkenes demonstrate a free-radical process.[18] The first step in this reaction is a dissociation of $[(P)Rh]_2$ to form (P)Rh. This monomeric Rh^{II} species has been reported in many studies.[6,11,17,23–25] It has never been isolated but its optical spectrum has been recorded at 77 K.[26]

An iridium(II) octaethylporphyrin dimer can be synthesized by photolysis of $(OEP)Ir(CH_3)$[12] (Eq. (3)). The physicochemical data of $[(OEP)Ir]_2$ are analogous to data reported for $[(OEP)Rh]_2$ and are characteristic of a complex with an $Ir^{II}–Ir^{II}$ bond.

$$2(OEP)Ir(CH_3) + C_6D_6 \xrightarrow{h\nu} [(OEP)Ir]_2 + CH_3D + CH_3C_6D_5 \quad (3)$$

Several organometallic reactions of $[(OEP)Ir]_2$ have been studied and are summarized in Scheme II.

Oxidative addition of H_2 and alkyl C–H bonds as well as alkene insertion reactions can occur. Oxidative addition to $[(OEP)Ir]_2$ leads to the hydride (OEP)IrH. This compound can then react with an excess of aldehyde to form α-hydroxyalkyl complexes of the type (OEP)Ir[CH(OH)R] where R = H or CH_3. These reactions are similar to reactions described above for $[(OEP)Rh]_2$ and it is thus postulated that a homolytic dissociation of the $Ir^{II}–Ir^{II}$ bond will give the transient metallo-radical $(OEP)Ir^{\bullet}$. Selective reactions with methyl C–H bonds are shown to be compatible with a metallo-radical mechanism.

1.B. Double Bonded Homodimers

Binuclear Ru^{II} and Os^{II} porphyrin dimers of the form $[(P)M]_2$ have been prepared by vacuum pyrolysis of the mononuclear bis(pyridine) complexes $(P)M(py)_2$, according to Eq. (4) where P = OEP or TPP and M = Ru^{II} [13,27] or Os^{II}.[6]

$$2(P)M(py)_2 \xrightarrow[\text{vacuum}]{\Delta} [(P)M]_2 + 4\ py \qquad (4)$$

X-ray and NMR results of the Ru(II) porphyrin dimer $[(OEP)Ru]_2$ are consistent with a qualitative MO diagram that suggests a formal Ru–Ru bond order of 2.[27] The highly air sensitive ruthenium and osmium dimers readily bind a wide variety of ligands in the absence of oxygen and quantitatively give the corresponding monomeric ruthenium(II) bis-ligated porphyrins where the ligand, L, is THF (Eq. (5)).

$$[(P)M]_2 \xrightarrow{L} 2\ (P)M(L)_2 \qquad (5)$$

Neutral and reduced ruthenium porphyrin dimers can be used in the preparation of monomeric σ-bonded, carbene, or π complexes.[28-30] The reaction of reduced ruthenium and osmium porphyrin dimers of the form $[(P)M]^{-2}$ with alkyl iodide produces the dialkyl complexes $(P)M(R)_2$ where M = Ru or Os and R = CH_3 or CH_3CH_2 (Eq. (6)).

$$[(P)M]^{-2} + 2\ RI \longrightarrow (P)M(R)_2 + 2I^- \qquad (6)$$

The first step of the decomposition involves reversible homolysis of the ruthenium carbon bond which leads to the paramagnetic σ-bonded $(P)Ru(CH_2CH_3)$ derivative and to an ethyl radical when C_2H_5I is the alkylating reagent[30] (Eq. (7)). Addition of radical trap in excess permits the clean preparation of $(P)Ru(CH_2CH_3)$.

$$(P)Ru(CH_2CH_3)_2 \rightleftharpoons (P)Ru(CH_2CH_3) + {}^{\bullet}CH_2CH_3 \qquad (7)$$

Carbene complexes of ruthenium can be synthesized from the reaction of neutral $[(P)Ru]_2$ dimers[30] with the diazoalkanes N_2CHR where R = CH_3 or $CO_2CH_2CH_3$ (Eq. (8)).

$$[(P)Ru]_2 \xrightarrow{N_2CHR} 2(P)Ru[CH(R)] + 2\ N_2 \qquad (8)$$

The carbene complexes ((P)Ru[CHSi(CH_3)$_3$] and (P)Ru[C=C(p-C_6H_4Cl)$_2$]) can also be isolated by reacting the [(P)Ru]$^{-2}$ dianion with geminal dihalides.[28]

The reaction of [(P)Ru]$^{-2}$ with methylene chloride in THF gives a mixture of two compounds, the π complexes (P)Ru($CH_2{=}CH_2$) and (P)Ru(THF)$_2$ (Eq. (9)). The same derivatives are also formed when the neutral [(P)Ru]$_2$ dimer reacts with N_2CH_2. This suggests that the two reactions involve a carbene (P)Ru(CH_2) intermediate.

$$2[(P)Ru]^{-2} \xrightarrow{CH_2Cl_2,THF} (P)Ru(CH_2{=}CH_2) + (P)Ru(THF)_2 \quad (9)$$

Treatment of [(P)Ru]$^{-2}$ or [(P)Os]$^{-2}$ with 1,2-dibromoethane yields the same π derivative (P)M($CH_2{=}CH_2$) where M = Ru or Os (Eq. 10).

$$[(P)M]^{-2} \xrightarrow{BrCH_2CH_2Br} (P)M(CH_2{=}CH_2) \quad (10)$$

The reaction of [(P)Ru]$_2$ with ethylene in THF also gives (P)Ru ($CH_2{=}CH_2$).

The ruthenium and osmium metalloporphyrin dimers are easily cleaved by coordinating ligands to produce the monomeric bisligated complexes, (P)M(L)$_2$. Similarly, [(P)Ru]$_2$ and [(P)Os]$_2$ react with bridging ligands such as pyrazine, 4,4′-bipyridine, and 1,4-diazabicyclo[2.2.2]octane to give linear polymers as shown in Eq. (11).[31-33]

$$n/2[(P)M]_2 + n\text{L–L} \rightarrow [(P)M(\text{L–L})]_n \quad (11)$$

The extent of polymerization is determined from the ratio of the absorbance for the pyrazine ν_{8a} mode of the bis(pyrazine) monomer to the absorbance of the μ-pyrazine polymer. Typical chain lengths of polymeric [(P)M(pyr)]$_n$ are $n = 25$ (± 5) for ruthenium, and $n = 20$ (± 5) for osmium.

The coordination polymers can be oxidized with a nonstoichiometric amount of oxidant ρ, where $0 < \rho < 1$ and lead to highly conductive solids (Eq. (12)).

$$[(P)M^{2+}(\text{L–L})] + \rho[A] \rightarrow [(P)M^{+2}_{(1-\rho)}\, M^{3+}_{\rho}(\text{L–L})](A^-)_\rho \quad (12)$$

The A^- anion serves to maintain charge neutrality. The conductivity of the polymer depends upon the extent of doping, the nature of the central transition metal and the bridging ligand. Various physicochemical measurements of the polymers, including electrochemical studies with carbon cloth electrodes, have been carried out and demonstrate that the doping reactions are metal-centered. This contrasts with other porphyrin conductors in which the conduction pathway is reportedly dominated by the macrocycle.[4]

The above results fit well with electrochemical data for oxidation and reduction of $[(OEP)Ru]_2$ and $[(OEP)Os]_2$.[34] The electrochemistry of these two dimers in dimethoxyethane and CH_2Cl_2 has been reported. Each compound can undergo up to two reductions and four oxidations. The second reduction is not observed in CH_2Cl_2 due to the proximity of this reaction to the potential for solvent discharge. The $[(OEP)Os]_2$ and $[(OEP)Ru]_2$ complexes contain Os^{II} and Ru^{II} central metals. The stepwise reduction of the dimers leads to the formation of an anion radical and a dianion with the electrons localized on both of the porphyrin rings. In contrast, oxidation of $[(OEP)Os]_2$ and $[(OEP)Ru]_2$ is postulated to occur at the central metal ions leading to the successive formation of dimers containing M^{II}/M^{III}, M^{III}/M^{III}, M^{III}/M^{IV} and M^{IV}/M^{IV} units. This behavior is quite different from that of $[(TPP)Rh]_2$ which undergoes only a single two-electron reduction step and cleaves to generate $[(TPP)Rh]^+$ after electrooxidation.[11]

1.C. Quadruple Bonded Homodimers

The molybdenum(II) porphyrin dimer $[(OEP)Mo]_2$ is the only known quadruply bonded homodimer[14] and is obtained by vacuum pyrolysis of the π bonded acetylene complex $(OEP)Mo(PhC{\equiv}CPh)$ (Eq. (13)).

$$2(OEP)Mo(PhC{\equiv}CPh) \xrightarrow[\text{vacuum}]{\Delta} [(OEP)Mo]_2 + 2PhC{\equiv}CPh \qquad (13)$$

Molybdenum(II) dimers are also obtained by heating a mixture of $MoCl_2(CO)_4$ and $(P)H_2$ where P is OEP, α-CHO-OEP, α-NH_2-OEP, α-NCO-OEP or α, γ-CH_3-Etio (Eq. (14)).

$$2(P)H_2 + 2\,MoCl_2(CO)_4 \longrightarrow [(P)Mo]_2 \qquad (14)$$

^1H NMR studies of the meso-substituted derivatives provide good evidence for a barrier to rotation about the metal–metal bond. The activation energy for this rotational process is 10.1 ± 0.5 kcal mole^{-1}. This is a measure of the σ-bond strength and confirms the existence of the Mo–Mo quadruple bond.

1.D. Single and Multiple Bonded Heterodimers

The single bonded heterodimer (OEP)RhIn(OEP) is synthesized by reaction of (Na)[(OEP)Rh] with (OEP)InCl.[35] This nucleophilic substitution is analogous to the method reported for synthesis of single bonded complexes containing one porphyrin unit.[36,37] The interplanar separation of 3.41 Å in (OEP)RhIn(OEP) is relatively long compared to the 3.26 Å separation for $[(OEP)Ru]_2$ and suggests that there is little interaction between the In and Rh porphyrin ligands units. Also, in contrast to the single bonded homodimer, $[(OEP)Rh]_2$,[8,9,38–40] the single bonded heterodimer fails to react thermally or photolytically with a dihydrogen carbon monoxide, or with phenylacetylene, acrylonitrile, triethylphosphite, *n*-butylisocyanide, or dioxygen.[4] A polar Rh^{I}–In^{III} bond is suggested to explain the absence of any reaction with donor molecules. The $[(OEP)Rh]^-$ fragment reacts as an electron donor with alkyl iodide according to Eq. (15) where R = CH_3 or CH_2CH_3.

$$\text{(OEP)RhIn(OEP)} + \text{RI} \rightarrow \text{(OEP)Rh(R)} + \text{(OEP)InI} \quad (15)$$

The electron donor properties of $[(OEP)Rh]^-$ are also evidenced by the rapid Rh–In bond cleavage by HX where X = O_2CCH_3, O_2SCF_3, or O_3SCF_3. The products of this reaction are the corresponding (OEP)RhH and (OEP)InX species (Eq. (16)).

$$\text{(OEP)RhIn(OEP)} + \text{HX} \rightarrow \text{(OEP)RhH} + \text{(OEP)InX} \quad (16)$$

The double bonded (OEP)Ru═Os(OEP) heterodimer has been described.[6] This derivative is obtained by reacting the two corresponding metalloporphyrin monomers which have their central metals in the same oxidation state. (OEP)Ru═Os(OEP) was only characterized by its NMR spectrum.

2. SINGLE σ-BONDED HETERONUCLEAR COMPLEXES OF THE TYPE (P)MM′(L) OR $[(P)In]_2Fe(CO)_4$

2.A. Single σ-Bonded Complexes Containing One Porphyrin Unit

Various indium–metal[36,37] and thallium–metal[41] bonded porphyrin complexes have been synthesized. These complexes are represented by (P)InM′(L) and (P)TlM′(L) where P is OEP or TPP and M′(L) is one of a number of different metalate species. The syntheses of these derivatives can be accomplished by three different methods. The first method involves nucleophilic substitution of the chloride ion on (P)InCl or (P)TlCl by M′(L) where M′(L) is $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$, $[Cr(CO)_3Cp]^-$, $[Mo(CO)_3Cp]^-$ or $[W(CO)_3Cp]^-$ (Eq. (17)).

$$(P)MCl + [M'(L)]^- \rightarrow (P)MM'(L) + Cl^- \qquad (17)$$

Yields obtained by this method vary between 20 and 70% and suggest the following classification of the metalate anion reactivity:

$$[Co(CO)_4]^- < [Cr(CO)_3Cp]^- < [Mo(CO)_3Cp]^- \approx [Mn(CO)_5]^- < [W(CO)_3Cp]^-$$

For porphyrins in the indium series, this agrees with a classification based on the nucleophilic power of the anion.[42]

The second synthetic method involves a photochemical reaction of the aryl or alkyl σ-bonded indium porphyrin and dimeric $Co_2(CO)_8$ or $[Mo(CO)_3Cp]_2$ (Eq. (18)). The formation of a $(P)In^9$ radical species during the reaction is demonstrated by ESR spectroscopy. Also, all attempts to prepare the corresponding thallium derivatives by this method have been unsuccessful.

$$(P)In(R) \xrightarrow[h\nu]{[M'(L)]_2} (P)InM'(L) \qquad (18)$$

The third synthetic method only works for the synthesis of $(P)InCo(CO)_4$ and proceeds via a reaction involving (P)InCl and

$Co_2(CO)_8$ in THF. The nature of the solvent is important since the reaction is only observed to occur in THF.

The X-ray structures of (OEP)InMn$(CO)_5$ [37] and (OEP)TlMn $(CO)_5$ [41] have been determined. The two derivatives are isotypic but the metal–metal bonding characteristics are slightly different. The metal–metal distance is shorter in (OEP)TlMn$(CO)_5$ than in (OEP)InMn$(CO)_5$ but the central metal atom is more out of plane in (OEP)TlMn$(CO)_5$ than in (OEP)InMn$(CO)_5$.* The same changes are observed between the indium and thallium series when a Mo$(CO)_3$Cp group is coordinated to the central metal.[43] These studies provide further evidence for a single metal–metal σ bond in the (P)InM'(L) and (P)TlM'(L) complexes, and also show the structural effect of the nature of the axial metalate ligand. Although the chemical reactivity of $[Mn(CO)_5]^-$ and $[Mo(CO)_3Cp]^-$ are similar, the cyclopentadienyl group leads to complexes with a longer metal–metal bond and a large porphyrin metal displacement above the plane of the four nitrogens. Consequently, the metal–metal bond is weaker in the (P)MM'$(CO)_3$Cp complexes.

The ratio of molar absorptivities (ϵ(II)/ϵ(I)) for the split Soret bands I and II of (P)InM'(L) and (P)TlM'(L) varies as a function of both the porphyrin macrocycle and the axial M'(L) ligand. The magnitude of the ratio reflects the degree of electron transfer from metal (indium or thallium) to the porphyrin macrocycle. The sensitivity of ϵ(II)/ϵ(I) to changes in the porphyrin macrocycle or axial ligand is larger for complexes in the (P)InM'(L) series than for those in the (P)TlM'(L) series. The larger displacement of the thallium ion from the mean plane in (P)TlM'(L) compared to that of the indium ion in (P)InM'(L)* can explain this difference. Moreover, the electron transfer from the thallium ion is smaller than from the indium atom even if the nature of the thallium–metal bond is more covalent as shown by the calculated residual charge.[43]

A detailed electrochemical study of (P)TlM'(L) and (P)InM'(L) has been carried out and the overall reduction and reoxidation sequence involving these complexes is given in Scheme III.

---

*(OEP)MMn$(CO)_5$: In–Mn = 2.705(1) Å, Tl–Mn = 2.649(1) Å, $\Delta 4N_{In}$ = 0.744(1) Å, $\Delta 4N_{Tl}$ = 0.939(1) Å. (OEP)MMo$(CO)_3$Cp: In–Mo = 2.890(1) Å, Tl–Mo = 2.829(1) Å, $\Delta 4N_{In}$ = 0.791(1) Å, $\Delta 4N_{Tl}$ = 1.00(0) Å ($\Delta 4N$ = distance (Å) from the plane of the four nitrogen atoms).

$$\begin{tikzcd}[column sep=small]
\text{Reductive scan:} & (P)MM'(L) \arrow[r, shift left, "+e"] & \left[(P)MM'(L)\right]^{\bullet -} \arrow[l, shift left] \arrow[r, shift left, "+e"] \arrow[d, "-{[M'(L)]^-}"] & \left[(P)MM'(L)\right]^{-2} \arrow[l, shift left] \arrow[d, "-{[M'(L)]^-}"] \\
 & & (P)M^{\bullet} & \left[(P)M\right]^-
\end{tikzcd}$$

Reoxidation:

$$[(P)M]^- \rightleftharpoons (P)M^\bullet + e^-$$

$$(P)M^\bullet \rightleftharpoons [(P)M]^+ + e^-$$

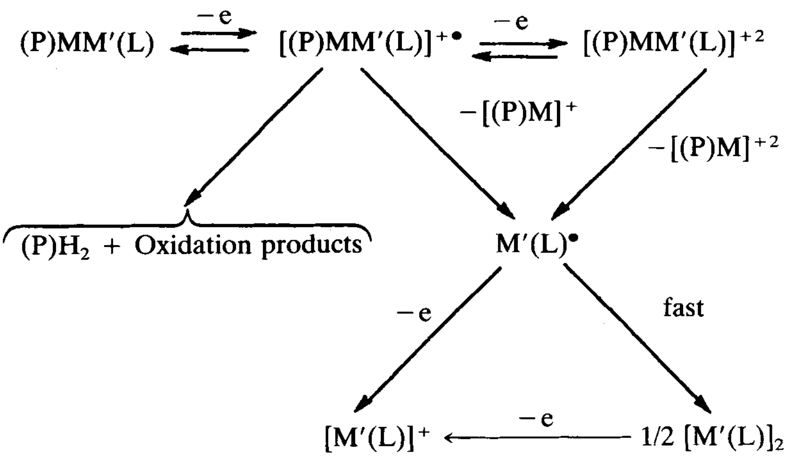
$$[M'(L)]^- \rightleftharpoons 1/2\ [M'(L)]_2 + e^-$$

SCHEME III

Reduction of binuclear (P)MM'(L) can occur by one or two electrons depending upon the specific porphyrin ring, the temperature, the nature of M, and the nature of the bound metalate ion, M'(L). Additional peaks may also be observed for oxidation and reduction of $(P)M^\bullet$ and $[(P)M]^-$ which are formed by cleavage of the reduced bimetallic species, as well as for $[(P)M]^+$ when some decomposition of the neutral complex occurs. The generated anion radical stability is very low for complexes in both the Tl and the In series. The ultimate products of (P)TlM'(L) electroreduction are the free base porphyrin radical anion and a bis-thallium(I) compound, $(P)Tl_2$, which is formed from a transient mono-thallium(I) complex, $[(P)Tl^{I}]^-$.

Electrochemical and spectroscopic data for electrooxidation of the (P)MM'(L) complexes are consistent with the overall mechanism summarized in Scheme IV.

Each (P)MM'(L) complex undergoes two oxidations which are centered at the porphyrin π ring system. Unlike binuclear complexes in the indium series, no cleavage of the Tl–M' σ-bond occurs following the first oxidation of (P)TlM'(L), i.e., the generated radical cations are stable on the cyclic voltammetry time scale. These results show that the Homo orbitals belong essentially to the macrocycle whatever the porphyrin metal, but that the σ and π porphyrin orbitals are closer in energy for the indium complexes than for the thallium derivatives. This results in a shorter



SCHEME IV

metal–metal bond length and a stability of both the neutral and the singly or doubly oxidized (P)TlM'(L) complexes.

Initial attempts to isolate similar gallium–metal complexes were unsuccessful, but (P)GaRe$(CO)_5$ has recently been synthesized and its characterization is underway.[44]

Octaethylporphinatorhodium dimers react with dimeric $[Mn(CO)_5]_2$, $[Mo(CO)_3Cp]_2$ and $[Ru(CO)_2Cp']_2$ to form the metathesis products (OEP)RhM'(L) where M'(L) is $Mn(CO)_5$, $Mo(CO)_3Cp$, or $Ru(CO)_2Cp'$ (Cp = η^5-C_5H_5; Cp' = η^5-$C_5(CH_3)_5$)[45] (Eq. (19)).

$$[(OEP)Rh]_2 + [M'(L)]_2 \rightarrow 2(OEP)RhM'(L) \qquad (19)$$

These heterobimetallic derivatives react with H_2 and CO to produce M'(L)H and equilibrium quantities of (OEP)RhH and (OEP)Rh(CHO).

2.B. Single σ-Bonded Complexes Containing Two Porphyrin Units

The only known derivatives of this type are the $[(P)In]_2Fe(CO)_4$ complexes where P is OEP or TPP.[36,46] Three different synthetic methods have been utilized for preparation of these trinuclear complexes. The first involves nucleophilic substitution of the chloride ion on (P)InCl by $[Fe(CO)_4]^{-2}$ which is generated by Collman's reagent (Eq. (20)).

$$2(P)InCl + [Fe(CO)_4]^{-2} \rightarrow [(P)In]_2Fe(CO)_4 + 2Cl^- \quad (20)$$

The second synthetic method involves a photochemical reaction of the methyl σ-bonded porphyrin $(P)In(CH_3)$ and dimeric $Fe_2(CO)_9$ (Eq. (21)). During this reaction, an intermediate $(P)In[Fe(CO)_4](CH_3)$ species is formed which decomposes to give the corresponding trinuclear complex. The reaction proceeds in the first step via a mechanism similar to that of an insertion reaction.

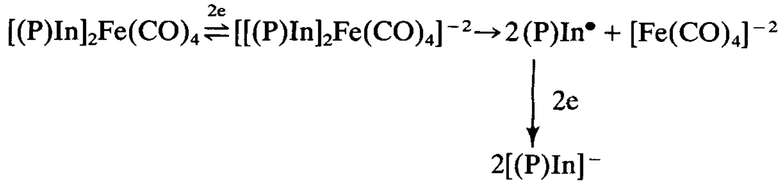
$$(P)In(CH_3) \xrightarrow{Fe_2(CO)_9} (P)In[Fe(CO)_4](CH_3) \longrightarrow [(P)In]_2Fe(CO)_4 \quad (21)$$

The last method proceeds via a reaction involving the hydride $[HFe(CO)_4]^-$ and (P)InCl (Eq. (22)).

$$(P)InCl + [HFe(CO)_4]^- \rightarrow (P)In[Fe(CO)_4]H \rightarrow [(P)In]_2Fe(CO)_4 \quad (22)$$

A transient species of the form $(P)In[Fe(CO)_4]H$ has been characterized by spectroscopic measurements. The spectroscopic data also demonstrate that the (P)In units are trans-coordinated with regard to the planar $[Fe(CO)_4]^{-2}$ ligand. As previously mentioned for the binuclear (P)InM'(L) complexes,[36,37] the presence of one extra band in the Soret region of the UV-visible spectrum of $[(P)In]_2Fe(CO)_4$ can be attributed to the electron donating character of the $Fe(CO)_4$ ligand which increases the electron charge density on indium.

The $[(P)In]_2Fe(CO)_4$ complexes have been studied by electrochemical methods. The complexes can be reduced by two electrons, but a rapid cleavage of the metal–metal bonds occurs leading to formation of $(P)In^\bullet$ and $[Fe(CO)_4]^{2-}$. Further reduction of $(P)In^\bullet$ gives the monoanion $[(P)In]^-$. This mechanism is presented in Scheme V.



$$\begin{tikzcd}[column sep=small] {[(P)In]_2Fe(CO)_4} \arrow[r, shift left, "2e"] & {[[(P)In]_2Fe(CO)_4]^{-2}} \arrow[l, shift left] \arrow[r] & {2(P)In^{\bullet}} \arrow[d, "2e"] & {+\ [Fe(CO)_4]^{-2}} \\ & & {2[(P)In]^{-}} & \end{tikzcd}$$

SCHEME V

The $[(P)In]_2Fe(CO)_4$ complexes can also be electroxidized but undergo a rapid cleavage of the metal–metal bonds after the first oxidation step which corresponds to a two electron abstraction (Eq. (23)).

$$[(P)In]_2Fe(CO)_4 \overset{-2e}{\rightleftharpoons} [[(P)In]_2Fe(CO)_4]^{+2} \rightarrow 2[(P)In]^{+2} + [Fe(CO)_4]^{-2} \qquad (23)$$

The electrochemical results show that there is no interaction between the two porphyrin macrocycles of $[(P)In]_2Fe(CO)_4$ and that the metal–metal bond is also relatively weak. Indeed, the initial oxidation or reduction of the trinuclear complex is followed by a rapid cleavage of the metal–metal bond. This result confirms deductions made on the basis of spectral data and demonstrates that the two metalloporphyrin units of the complexes are equivalent with no interaction occurring across the $Fe(CO)_4$ bridge. Thus, the properties of $[(P)In]_2Fe(CO)_4$ differ from those of the carbenoid bonded $(P)SnFe(CO)_4$ and $(P)GeFe(CO)_4$ complexes which are discussed in the next section.

3. CARBENOID BONDED HETERONUCLEAR METALLOPORPHYRINS

3.A. Bimetallic Donor–Acceptor Complexes of the Type (P)MM′(L)

Bimetallic donor–acceptor complexes can be formed with tin and germanium porphyrins as shown in Eq. (24).[47–49] The reaction of

$Na_2Fe(CO)_4$ with $(P)SnCl_2$ or $(P)GeCl_2$ produces the $(P)MFe(CO)_4$ derivatives where P is OEP, TpTP or TmTP and M is Sn or Ge.

$$(P)MCl_2 \xrightarrow{Na_2Fe(CO)_4} (P)MFe(CO)_4 \qquad (24)$$

Sn^{II} and Fe^0 oxidation states have been assigned to the metal ions in $(P)MFe(CO)_4$ on the basis of various spectral data, including Mössbauer spectra.[47]

$(OEP)SnFe(CO)_4$ has been studied by X-ray methods and the length of the Sn–Fe bond found to be 2.492(1) Å. The tin–iron bond is short, as expected, and represents the first example of a carbenoid metal–metal bond in metalloporphyrin chemistry. The (OEP)Sn unit can be considered as a σ-donor which enhances the 4s electron occupation of the iron atom. By analogy, the (P)Ge $Fe(CO)_4$ complexes are also postulated to have the main-group metal in a low oxidation state. As such, the metalloporphyrin would contain a Ge^{II}–Fe^0 metal–metal bond.

Sn^{II} and Ge^{II} oxidation states are extremely uncommon in metalloporphyrins. In fact, no Ge^{II} porphyrins have ever been reported. Several spectral characterizations of tin(II) porphyrins of the type (OEP)Sn[50] and (TPP)Sn[51] have appeared in the literature, but it is only recently that a genuine sample of air stable (TPP)Sn has been isolated.[52] Thus, the carbenoid metal–metal bonded metalloporphyrin complexes are unique in that the main-group metal is air stable in the low oxidation state.

The electrochemistry of the $(P)MFe(CO)_4$ complexes have also been studied. These bimetallic complexes are extremely stable after electroreduction and two reversible one-electron transfer steps can occur without cleavage of the metal–metal bond. Both reductions seem to occur at the porphyrin π ring system. The difference in $E_{1/2}$ between reduction of the $(P)SnFe(CO)_4$ and $(P)GeFe(CO)_4$ complexes with the same porphyrin ring ranges between 20 and 70 mV with the former complexes being the easiest to reduce. This is consistent with the slightly higher electronegativity of Ge^{II} (2.01) with respect to Sn^{II} (1.96) and suggests that the site of electroreduction occurs at the porphyrin π ring system. This conclusion is also suggested by results of thin-layer spectroelectrochemistry and controlled potential electrolysis coupled with ESR.

Each $(P)MFe(CO)_4$ complex undergoes an irreversible oxidation which leads to $Fe_3(CO)_{12}$ and the tin(IV) or germanium(IV) $[(P)M]^{+2}$ species as the main products after the global abstraction of two electrons. Evidence for the above oxidation products also comes from the coulometric value of the number of transferred electrons. A self-consistent mechanism for the coupled chemical and electrochemical steps in the electrooxidation is presented in Scheme VI.

$$(P)MFe(CO)_4 \xrightarrow{-2e} [(P)MFe(CO)_4]^{+2}$$

$$[(P)MFe(CO)_4]^{+2} \longrightarrow [(P)M]^{+2} + Fe(CO)_4$$

$$Fe(CO)_4 \longrightarrow 1/3\ Fe_3(CO)_{12}$$

SCHEME VI

3.B. Polymetallic Donor–Acceptor Complexes of the Type $(P)Sn[Mn(CO)_4HgMn(CO)_5]$ and $(P)Sn[Co(CO)_3MCo(CO)_4]$

$(TPP)Sn[Mn(CO)_4HgMn(CO)_5]$ is formed by reaction of $(TPP)SnCl_2$ with $Hg(Mn(CO)_5)_2$ according to Eq. (25).[53,54]

$$(TPP)SnCl_2 \xrightarrow{Hg[Mn(CO)_5]_2} (TPP)Sn[Mn(CO)_4HgMn(CO)_5] \quad (25)$$

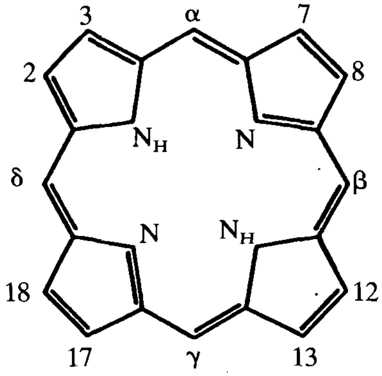
The tin–manganese distance in $(TPP)Sn[Mn(CO)_4HgMn(CO)_5]$ is short (2.554(7) Å) and the tin atom lies 0.85 Å above the plane of the four porphyrin nitrogens.[53] This is similar to the structure of $(OEP)SnFe(CO)_4$.[47] The fact that the Sn–Mn and Mn–Hg bonds (Mn–Hg distance of 2.582(3) Å in $(TPP)Sn[Mn(CO)_4HgMn(CO)_5]$) are shorter than ordinary Sn–Mn and Mn–Hg bonds can be explained in terms of the π back-donation from the Mn atom to the Sn and Hg atoms.

The reaction of $(TPP)SnCl_2$ with $M[Co(CO)_4]_2$ gives $(TPP)Sn[Co(CO)_3MCo(CO)_4]$ where M = Zn, Cd or Hg[53,54] (Eq. (26)).

$$(TPP)SnCl_2 \xrightarrow{M[Co(CO)_4]_2} (TPP)Sn[Co(CO)_3MCo(CO)_4] \quad (26)$$

The physicochemical properties of these complexes are similar to those of the carbenoid complexes. However, no electrochemical data is available to date.

4. NOMENCLATURE



Abbreviation	Name	Substituents								
		2	3	7	8	12	13	17	18	α,β,γ,δ
P	Porphine	H	H	H	H	H	H	H	H	H
OEP	Octaethylporphyrin	Et	Et	Et	Et	Et	Et	Et	Et	H
TPP	Tetraphenylporphyrin	H	H	H	H	H	H	H	H	Ph
TmTp	Tetra-m-tolylporphyrin	H	H	H	H	H	H	H	H	mT
TpTP	Tetra-p-tolylporphyrin	H	H	H	H	H	H	H	H	pT
Etio-I	Etioporphyrin-I	Me	Et	Me	Et	Me	Et	Me	Et	H
Etio-II	Etioporphyrin-II	Me	Et	Et	Me	Me	Et	Et	Me	H

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