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Some Aspects of Organometallic Chemistry in Metalloporphyrin Chemistry: Synthesis, Chemical Reactivity, and Electrochemical Behavior of Porphyrins with Metal–Carbon Bonds

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Contents

I. Synopsis

This review discusses the synthesis, physical properties, chemical reactivity, and electrochemistry of σ- and π-bonded porphyrin complexes. Transition- and non-transition-metal–carbon σ-bonded porphyrins with the following central metals have been synthesized: Fe, Ru, Os, Mo, Ni, Co, Rh, Ir, Ti, Al, Ga, In, Tl, Si, Ge, Sn, and Zn. Transition-metal porphyrins with π-bonded ligands have also been isolated. These include both axially symmetrical complexes of iron and ruthenium and axially unsymmetrical complexes of cobalt and nickel. Metalloporphyrin π complexes with Os, Mo, and Ru central metals have also been reported. The chemical reactivity of each complex is discussed as is the interest of these compounds as models for biological systems. The review attempts to show the fundamental importance of the porphyrin ligand in directing the reactivity and redox properties of the organometallic porphyrin complexes while focusing on the following points: (i) Synthetic procedures and reactivity of σ-bonded iron–alkyl and iron–aryl porphyrins and iron–carbene porphyrins are presented. These type complexes are formed during the metabolism of certain substrates by cytochrome P-450, and thus studies of reversible migrations between the central metal and one pyrrolic nitrogen of synthetic cobalt and iron porphyrins are related to similar biological reactions. (ii) The synthesis and chemical and electrochemical properties of ruthenium, osmium, cobalt, and rhodium, and iridium complexes are reviewed. The original synthetic routes involving metalloporphyrin dimers and the versatile reactivity of σ-bonded ruthenium, rhodium, and iridium porphyrins are presented. (iii) Special emphasis is placed on the electrochemical behavior of indium and gallium porphyrins. This review also covers new developments in the series of σ-bonded aluminum and thallium porphyrins as well as other σ- and π-bonded metalloporphyrins that are not described in the initial sections.

II. Introduction

Porphyrins are known to coordinate with most metallic or pseudometallic elements, and the synthesis of numerous different organometallic porphyrin derivatives containing one or more metal–carbon bonds is possible. However, to date, the synthesis of metal–carbon complexes has been limited to metalloporphyrins with the following central metals: Fe, Ru, Co, Rh, Ir, Mo, Al, Ga, Ti, Os, Ni, In, Tl, Si, Ge, Sn, and

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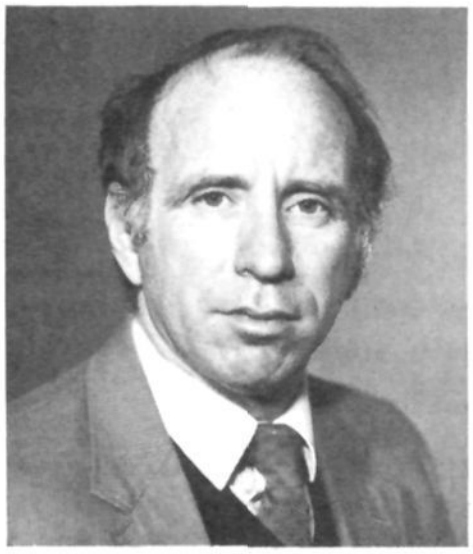

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Zn. These types of organometallic complexes are of importance as model compounds for understanding the functions and relationships of several biologically important macromolecules, as well as for their chemical reactivity. In this regard, σ-bonded iron–alkyl and iron–aryl porphyrins as well as iron–carbene porphyrins have been the subject of extensive studies involving synthesis, spectrochemical, and electrochemical characterization. These compounds were proposed to occur during the metabolism of various substrates by cytochrome P-450,[1-3] and this has led to the preparation of various models as well as to in vivo experiments that have demonstrated the involvement of iron–carbon species.

Although the biological implications of iron–carbon porphyrins can explain, in part, the numerous recent papers that have focused on synthetic metal–carbon bonded porphyrins, a development of the organometallic porphyrin chemistry in the iron and cobalt porphyrin triads is of another origin and is related to the rich chemistry and reactivity of these organometallic derivatives.

The synthesis, chemical properties, and characterization of transition- and non-transition-metal–carbon and metal–metal bonded porphyrins have been widely described during the past several half-dozen years.[4,5] Most of the complexes are obtainable from the usual reactions of chloro- or dichlorometalloporphyrins with alkyllithium or alkylmagnesium halides. The corresponding mono- or dialkyl derivatives are generally isolated in a good yield, depending upon the nature of the metal. However, an alternative synthesis used in organometallic chemistry is the reaction of low-valent organometallic derivatives with alkyl halides. This approach has been used for the preparation of σ-bonded metal–alkyl porphyrins of Fe, Co, Rh, and Ir. Iron(II) and rhodium(II) complexes undergo oxidative addition with alkylating agents via a one-electron-transfer process. Other synthetic procedures to obtain σ-bonded porphyrins have also been reported for complexes in specific metal series and involve the use of various reagents or metalloporphyrin dimers in the reactions. Aluminum and thallium porphyrins containing a metal–carbon bond are synthesized by treating the metal free porphyrins with organometallic compounds such as triethylaluminum or thallium methyl dihalide. Details for each of these reactions are discussed in the review.

Porphyrins with metal–carbon bonds are involved in many typical organometallic reactions. For example, the insertion of small molecules between the metal ion and the carbon atom of a metalloporphyrin may result in activation of the inserted molecule or may generate new monomeric or polymeric materials. In addition, σ-bonded metal–carbon porphyrins can act as precursors in the synthesis of metal–metal bonded derivatives. Moreover, the isolation of rare representatives in several metal series suggests the possibility of synthesizing a large number of additional novel organometallic porphyrin derivatives.

This review will cover the synthesis, chemical reactivity, and electrochemical behavior of transition- and non-transition-metal organometallic porphyrin complexes. The work is divided into sections on iron (section III), ruthenium and osmium (section IV), cobalt, rhodium, and iridium (section V), group 13 metals (section VI), and group 14 metals (section VII). Most of the described metalloporphyrins are σ-bonded by one alkyl or one aryl group and have a central metal ion in the +3 oxidation state. However, the group 14 complexes contain a central metal ion in the +4 oxidation state and are σ-bonded either with two alkyl or two aryl groups or alternatively with one σ-bonded ligand and one ionic ligand.

III. Iron-Alkyl, Iron-Aryl, and Iron-Carbene Porphyrins

A. Synthesis, Reactivity, and Properties of σ-Bonded Iron-Alkyl and Iron-Aryl Porphyrins

σ-Bonded alkyl, aryl, and perfluoroaryl iron(III) porphyrins have been obtained by reaction of (P)FeCl either with Grignard reagents or with alkyl- or aryllithium.[6-15] This reaction is given by eq 1, where M′ =

$$(\mathrm{P})\mathrm{FeCl} + \mathrm{RM'Y} \rightarrow (\mathrm{P})\mathrm{Fe(R)} + \mathrm{ClM'Y} \qquad (1)$$

Mg and Y = halide or where M′ = Li and there is no Y group.

The reaction of low-valent organometallic derivatives with alkyl or aryl halides is a classical synthetic method in organometallic chemistry and has also been used to synthesize σ-bonded iron porphyrins. The reaction of electrochemically generated iron(I) porphyrins and aryl or vinyl halides leads to σ-bonded iron(III) porphyrin complexes[16-18] as shown in eq 2. Kinetic measurements

$$[(\mathrm{P})\mathrm{Fe^I}]^- + \mathrm{R(Ar)X} \rightarrow (\mathrm{P})\mathrm{Fe^{III}[R(Ar)]} + \mathrm{X^-} \qquad (2)$$

of the substitution reaction in eq 2 indicate that the mechanism is more likely to have $\mathrm{S_N2}$ character than to be initiated by an electron-transfer reaction between Fe(I) and the alkyl halide.[16]

Iron(II) porphyrins undergo oxidative addition with alkylating agents via a monoelectronic process (reactions 3a and 3b).[19]

$$(\mathrm{P})\mathrm{Fe^{II}} + \mathrm{RX} \xrightarrow{\text{slow}} (\mathrm{P})\mathrm{Fe^{III}X} + \mathrm{R^\bullet} \qquad (3a)$$

$$\mathrm{R^\bullet} + (\mathrm{P})\mathrm{Fe^{II}} \xrightarrow{\text{fast}} (\mathrm{P})\mathrm{Fe^{III}(R)} \qquad (3b)$$

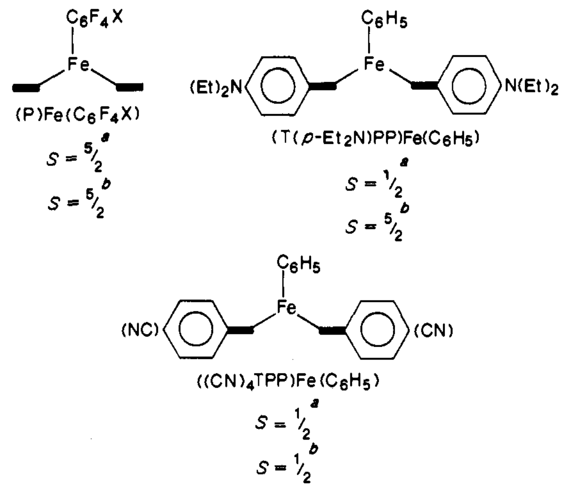
σ-Bonded iron-methyl porphyrins have been obtained by steady-state pulse radiolysis of methyl chloride saturated solutions containing ferric deuteroporphyrin or by chemical reduction of ferric deuteroporphyrin in a solution containing methyl iodide.[19] The reaction between iron-free deuteroporphyrin and methyl radicals is slow, thus implying that methyl radicals react at the iron porphyrin center. A transient $(\mathrm{DP})\mathrm{Fe^{IV}(CH_3)}$ species, if formed, could undergo a further slow reaction, leading to ferrous deuteroporphyrin (reaction 4).

$$[(\mathrm{DP})\mathrm{Fe^{III}}]^+ + \mathrm{CH_3^\bullet} \rightarrow [(\mathrm{DP})\mathrm{Fe^{IV}(CH_3)}]^+ \xrightarrow{\mathrm{OH^-}} (\mathrm{DP})\mathrm{Fe^{II}} + \mathrm{CH_3OH} \qquad (4a)$$

$$[(\mathrm{DP})\mathrm{Fe^{IV}(CH_3)}]^+ + (\mathrm{DP})\mathrm{Fe^{II}} \rightarrow (\mathrm{DP})\mathrm{Fe^{III}(CH_3)} + [(\mathrm{DP})\mathrm{Fe^{III}}]^+ \qquad (4b)$$

σ-Bonded alkyl and aryl iron(III) porphyrin complexes have spectral characteristics of paramagnetic species. Most σ-bonded iron-aryl or iron-alkyl porphyrins are described as low-spin complexes on the basis of ^{1}H NMR data.[11,13,16,20] However, the alkyl or aryl σ-bonded derivatives may exist as a mixture of high- and low-spin-state Fe(III) complexes. The iron center of (P)Fe(R) can also exhibit a high-spin state, depending on the nature of both the alkyl or aryl group and the equatorial ligand. For example, it has been demonstrated that the spin state of σ-bonded iron(III) porphyrins will vary as a function of the porphyrin ring basicity and/or the ligand field strength of the σ-bonded ligand.[15] Examples from this study are shown in Scheme 1, where X = H or F and P = OEP or TPP. σ-Bonded perfluoroaryl iron(III) complexes with electrophillic axial ligands exist as pure high-spin complexes, but complexes with more basic porphyrin ligands may exist in the high- or low-spin state, depending upon the experimental conditions. The $(\mathrm{CN})_4$TPP electron attractor ligand gives an iron-phenyl species with pure low-spin character.

SCHEME 1



[a] Spin value found by ^{1}H NMR in C_6D_6 at 298 K. [b] Spin value found by ESR in toluene at 115 K. Adapted from ref 15.

Table 1 lists ESR spectral characteristics of σ-bonded iron-alkyl and iron-aryl porphyrins at 115 K in toluene.[21] Several species have an ESR spectrum with three lines at g values close to 2 and two lines at g values near 2 and 6. The signals close to 2 are attributed to a low-spin-state Fe(III) species, while the signals at g = 2 and 6 are typical of a high-spin iron(III) species.[21]

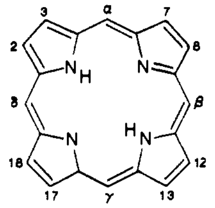
The specific spin state of the iron(III) complex will depend on parameters such as solvent, method of sample preparation, type of porphyrin ligand, and type of axial ligand. For example, the spin state of Fe(III) in (P)Fe(R) is critically dependent on the basicity of the porphyrin macrocycle. The metal-ligand bond strength decreases when the metal electron density or donor properties of the macrocycle increase. This is consistent with the following increasing order of porphyrin ligand basicity:

$$(\mathrm{CN})_4\mathrm{TPP} < \mathrm{TPP} \sim \mathrm{TpTP} \sim \mathrm{TmTP} < \mathrm{OEP} < \mathrm{T}(p\text{-}\mathrm{Et_2N})\mathrm{PP} \qquad (5)$$

Room-temperature ^{1}H NMR data of (P)Fe(R) are in agreement with low-spin entities for all of the complexes listed in Table 1 with the exception of the perfluoro derivatives. Analysis of chemical shifts for the σ-bonded iron-carbon derivatives were made[21] according to the method of LaMar and Walker[22] and the dipolar chemical shifts were determined.

It was demonstrated that the isotropic chemical shift $(\Delta H/H)^{\mathrm{iso}}$ for different proton sites of (TPP)Fe(p-$\mathrm{CH_3C_6H_4}$) vs T^{-1} was linear up to 273 K, thus demon-

TABLE 1



A. Nomenclature of Porphyrins

abbrev	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	C_6H_5
TmTP	tetra-*m*-tolylporphyrin	H	H	H	H	H	H	H	H	*m*-tolyl
TpTP	tetra-*p*-tolylporphyrin	H	H	H	H	H	H	H	H	*p*-tolyl
$T(pCF_3)PP$	tetrakis(*p*-(trifluoromethyl)phenyl)porphyrin	H	H	H	H	H	H	H	H	*p*-$CF_3C_6H_4$
$T(pEt_2N)PP$	tetrakis(*p*-(diethylamino)phenyl)porphyrin	H	H	H	H	H	H	H	H	*p*-$Et_2NC_6H_4$
TMP	tetramesitylporphyrin	H	H	H	H	H	H	H	H	2,4,6-$(CH_3)C_6H_2$
$(CN)_4TPP$	tetracyano-2,7,12,17-tetraphenylporphyrin	CN	H	CN	H	CN	H	CN	H	C_6H_5
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
MPIX	mesoporphyrin-IX	Me	Et	Me	Et	Me	${}_{P}H$	${}_{P}H$	Me	H
MPIXDME	mesoporphyrin-IX dimethyl ester	Me	Et	Me	Et	Me	Et	Me	Et	H
DP	deuteroporphyrin-IX	Me	H	Me	H	Me	P^{H}	P^{H}	Me	H
DPDME	deuteroporphyrin-IX dimethyl ester	Me	H	Me	H	Me	P^{Me}	P^{Me}	Me	H
PPIX	protoporphyrin-IX	Me	vinyl	Me	vinyl	Me	P^{H}	P^{H}	Me	H
PPIXDME	protoporphyrin-IX dimethyl ester	Me	vinyl	Me	vinyl	Me	P^{Me}	P^{Me}	Me	H

B. ESR Data of (P)Fe(R) in Toluene at 115 K[a]

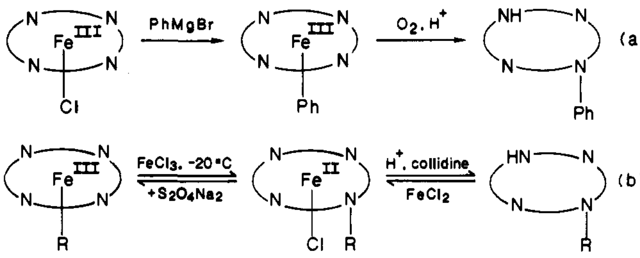
compd	$S = {}^1/_2$ g_x	g_y	g_z	Δ/λ	V/λ	V/Δ	$S = {}^5/_2$ $g_\perp$	$g_\parallel$
(OEP)Fe(*n*-C_4H_9)							5.99	1.99
(OEP)Fe(CH_3)							6.17	2.01
(OEP)Fe(C_6H_5)							6.31	1.99
(OEP)Fe(*p*-$CH_3C_6H_4$)							5.99	2.02
(TPP)Fe(*n*-C_4H_9)	1.90	2.28	2.56	5.20	3.85	0.74	6.10	1.98
(TPP)Fe(CH_3)	1.89	2.27	2.60	5.44	3.56	0.65	6.08	
(TPP)Fe(C_6H_5)	1.92	2.39	2.60	4.14	3.51	0.85	5.96	
(TPP)Fe(*p*-$CH_3C_6H_4$)	1.86	2.23	2.48	5.98	3.99	0.67	5.97	
(TmTP)Fe(*n*-C_4H_9)	1.89	2.27	2.52	5.03	3.99	0.79	6.45	1.99
(TmTP)Fe(CH_3)	1.87	2.28	2.61	5.02	3.46	0.69	6.02	1.99
(TmTP)Fe(C_6H_5)	1.86	2.25	2.55	5.11	3.65	0.71	6.02	1.98
(TpTP)Fe(*n*-C_4H_9)	1.88	2.27	2.53	4.94	3.88	0.78	6.26	1.98
(TpTP)Fe(CH_3)	1.88	2.30	2.57	4.65	3.72	0.80	6.08	
(TpTP)Fe(C_6H_5)	1.81	2.31	2.63	5.04	3.18	0.63	6.08	1.96
(T(*p*-Et_2N)PP)Fe(C_6H_5)							5.96	2.02
(($CN)_4$TPP)Fe(C_6H_5)	1.97	2.06	2.25	21.55	7.81	0.36		
(OEP)Fe(C_6F_4H)							5.88	1.98
(OEP)Fe(C_6F_5)							6.08[b]	1.97[b]
(TPP)Fe(C_6F_4H)							5.86	1.98
(TPP)Fe(C_6F_5)							5.86	1.99
(TmTP)Fe(C_6F_4H)							5.86	1.98
(TmTP)Fe(C_6F_5)							5.86	1.98
(TpTP)Fe(C_6F_4H)							5.81	1.98
(TpTP)Fe(C_6F_5)							5.85	1.98

[a] Data taken from ref 21. [b] In 2:1 toluene–methylene chloride mixtures.

strating that no low spin/high spin conversion occurs.[21] However, low-temperature ESR spectra of the (P)Fe(R) complexes in toluene and carbon disulfide indicated that the latter solvent induces a shift of the spin mixture toward the low-spin state and that the axial and equatorial ligand effects were predominant.[21] Furthermore, Raman spectroscopic data show that the iron atom is invariantly pentacoordinated independent of the solvent, the temperature, and the nature of the axial or macrocyclic ligands.[23] This implies that there is no coordination between the metal center and the solvent. Moreover, the ESR spectra of the (P)Fe(R) complexes greatly depend upon the method of sample preparation.[21] For example, grinding of the sample modifies the spin mixture such that the intensity of the high-spin signal increases while that of the low-spin signal decreases.

All pentacoordinate σ-bonded non-perfluoroaryl iron porphyrins should have the iron atom slightly out of the plane of the four nitrogen atoms. This was demonstrated for (TPP)Fe(C_6H_5) by X-ray[24] and EXAFS[25] studies, which show the iron atom to be 0.17 Å out of the nitrogen plane. The observed stabilization of the high-spin state may result from an expansion of the central hole and at the same time to a lengthening of the iron–carbon axial bond. However, the observed shift of the spin mixture is small and is only demonstrated by ESR spectroscopy.[21] The magnetic suscep-

SCHEME 2[a]



[a] (a) from ref 9; (b) from ref 27.

tibility and Mössbauer data do not show significant changes with grinding, thus indicating that grinding of the low-spin (P)Fe(R) samples modifies the molecular structure only at the surface of the sample.

Reactivity studies of σ-bonded iron porphyrins were first carried out in order to demonstrate that hemoglobin and myoglobin give rise to intermediate σ-bonded iron(III)–alkyl or iron(III)–aryl derivatives upon metabolic oxidation of hydrazines.[9,26-28] The final green *N*-phenylporphyrins result from an oxidative shift of the phenyl group from the metal to the heme nitrogen as the protein is denatured.

Two independent groups have demonstrated the chemically initiated reversible iron-to-nitrogen migration of alkyl, aryl, or vinyl groups in synthetic iron porphyrin model complexes.[9,27] These reactions are summarized in Scheme 2, where R is $CH{=}C(C_6H_5)_2$, CH_3, or C_6H_5.

Oxidation of (P)Fe(R) by $FeCl_3$ leads to the corresponding iron(II)-*N*-alkyl or -*N*-phenyl porphyrin complex.[27] This reaction is reversible and a reverse migration occurs after dithionite reduction of the generated N-substituted porphyrin.

Electrochemical and spectroelectrochemical studies showed that the migration could be electrochemically initiated and also suggested that the migration process occurred via an iron(IV) intermediate.[29] More recently, ^1H and ^2D NMR studies involving (P)Fe(R), where R = C_6H_5, p-$CH_3C_6H_4$, or m-$CH_3C_6H_4$, demonstrated that the corresponding phenyl iron(IV) porphyrin complexes could be produced by bromine oxidation of the σ-bonded tetraarylporphyrin iron(III) complexes at −60 °C in chloroform.[30] The identified porphyrins were characterized as iron(IV) species having an $S = 1$ spin state. This is consistent with a $d_{xy}{}^2d_{xz}{}^1d_{yz}{}^1$ orbital occupancy and the transfer of π-spin density from the porphyrin macrocycle to the axial group.

σ-Bonded iron porphyrins are able to undergo insertion reactions of small molecules. The insertion of sulfur dioxide between iron and the σ-bonded alkyl or aryl groups of iron–carbon porphyrins gives rise to sulfinato compounds. These compounds are air stable at room temperature but are easily oxidized by a stream of oxygen to give the corresponding sulfonato complexes (reaction 6).[31] The ^1H NMR spectra of $(P)Fe(SO_2R)$

$$(P)Fe(R) \xrightarrow{SO_2} (P)Fe(SO_2R) \xrightarrow[\text{toluene, }\Delta]{O_2} (P)Fe(SO_3R) \qquad (6)$$

and $(P)Fe(SO_3R)$ are characteristic of high-spin species. Their electronic absorption spectra are also similar to those of other high-spin iron(III) porphyrins belonging to the hyperclass.[32]

B. Synthesis, Reactivity, and Properties of Iron–Carbene Complexes

The preparation and properties of iron–carbene complexes were first reported by Mansuy et al.[33] $(TPP)Fe^{II}$ reacts with CCl_4 in the presence of excess iron powder under argon to give the $(TPP)Fe^{II}(CCl_2)$–carbene complex. The stoichiometry of this reaction is shown in eq 7. A structural determination of $(TPP)Fe(CCl_2)(H_2O)\cdot 2DMF$ has demonstrated the carbene nature of the coordinated ligand.[34] The 1.75-Å C–Cl distance is as expected for a C–Cl sp^2 bond, and the short Fe–C bond length of 1.73 Å is consistent with a double bond.

$$(TPP)Fe^{II} + CCl_4 + 2e^- \rightarrow (TPP)Fe(CCl_2) + 2Cl^- \qquad (7)$$

Various polyhalogenated compounds such as $X_3C(R)$ react with iron(II) porphyrins in the presence of excess reducing agents such as iron powder or sodium dithionite to give the corresponding (P)Fe(CXR) iron–carbene complexes. Iron–carbene complexes have also been synthesized with iron protoporphyrin-IX, which is present at the active site of several hemoproteins.[35] The same synthetic method has been utilized to prepare carbene complexes with electron-withdrawing substituents.[36] These reactions are summarized in eq 8, where X = Cl or Br and CXR = CCl_2,[33] CF_2,[35] CFCl,[35] CFBr,[35] CBr_2,[35] CCl(CN),[36] $CCl(COOC_2H_5)$,[36] and $CCl(CF_3)$.[35]

$$(P)Fe^{II} + X_3CR \rightarrow (P)Fe^{II}(CXR) \qquad (8)$$

All the iron–carbene porphyrins react irreversibly with dioxygen and nucleophiles such as pyridine or primary amines. The ability of the halogen substituent to stabilize the carbene complex toward oxidation increases in the order Br > Cl > F. The replacement of Cl by Br on the carbene ligand of $(P)Fe^{II}$ also enhances its rate of replacement by pyridine. Moreover, iron–carbene porphyrins with electron-withdrawing axial ligands such as CCl(CN), CCl(COOEt), or $CCl(CF_3)$ are considerably more reactive toward oxygen and nucleophiles than when the ligand is CCl_2. The relative stability of the carbene complexes bearing electron-withdrawing substituents has been explained by a stabilizing effect of the electron-rich porphyrin ligand.[35]

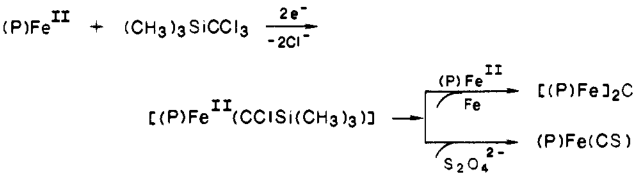
Attempts to prepare $(TPP)Fe(CI_2)$ from the reaction of CI_4 and (TPP)Fe were unsuccessful[37] but led to the μ-carbido dimer $[(TPP)Fe]_2C$ (reaction 9). The existence of two resonance forms involving iron(II) and iron(IV) oxidation states of $[(TPP)Fe]_2C$ have been proposed to explain its physicochemical properties.[37]

$$2(TPP)Fe + CI_4 + 4e^- \rightarrow [(TPP)Fe]_2C + 4I^- \qquad (9)$$

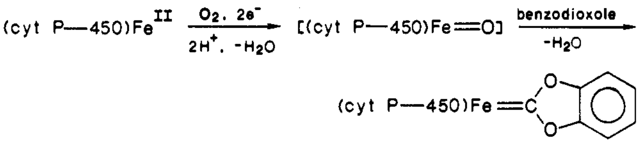
$$(TPP)Fe^{II}\leftarrow C\rightarrow Fe^{II}(TPP) \leftrightarrow (TPP)Fe^{IV}{=}C{=}Fe^{IV}(TPP) \qquad (10)$$

The μ-carbido porphyrin dimer has also been prepared by the reaction of (trichloromethyl)trimethylsilane with iron(II) tetraarylporphyrin when iron powder is used as a reducing agent. In this reaction the carbene (P)Fe(CClR) (where R = $Si(CH_3)_3$) is postulated to be a transient intermediate.[38] The (P)Fe(CS) derivative was isolated when the reducing agent was sodium dithionite[39] (Scheme 3). The binuclear carbene complex has a linear Fe–C–Fe bond and an Fe–C bond length of only 1.675 Å.[39]

SCHEME 3



SCHEME 4



The synthesis of (P)Fe(CXR) carbene complexes bearing electron donor R substituents has also been described.[35,40] Fungicides of the type $RXCCl_3$ where X = S or Se are reduced by Fe(II) porphyrins with formation of (P)Fe(CCl(SR)) carbene complexes. Treatment of these complexes with a Lewis acid leads to very stable thio- or selenocarbonyl iron porphyrins. These reactions are shown in eq 11, where X = S[35,40] or Se.[40]

$$(P)Fe^{II} + C_6H_5CH_2XCCl_3 \xrightarrow[-2Cl^-]{+2e^-} (P)Fe(CCl(XCH_2C_6H_5)) \rightarrow (P)Fe(CX) + C_6H_5CH_2Cl \tag{11}$$

The reaction of iron(II) porphyrins with $RCCl_3$ where R = CH_3 or CH_3CHOH also leads to the expected (P)Fe(CClR) carbene complexes.[35]

The insecticide $(p\text{-}ClC_6H_4)_2CHCCl_3$ (DDT) forms a very stable carbene complex upon reduction in the presence of $(P)Fe^{II}$ (eq 12).[41] The reaction gives

$$(p\text{-}ClC_6H_4)_2CHCl_3 + (P)Fe^{II} \xrightarrow[-2Cl^-,\ -HCl]{+2e^-} (P)Fe(C{=}C(p\text{-}ClC_6H_4)_2) \tag{12}$$

(P)Fe(CClR) but elimination of HCl leads to a vinylidene carbene complex. The final product in eq 12 is indefinitely stable to dioxygen, even in solution. It reacts with 1 equiv of $FeCl_3$ or $CuCl_2$ without an irreversible rupture of the Fe–carbene bond and gives rise to $(TPP)Fe^{III}(C{=}C(p\text{-}ClC_6H_4)_2Cl$.[35] Similar complexes are formed during reductive metabolism of the same chlorinated compounds by cytochrome P-450.

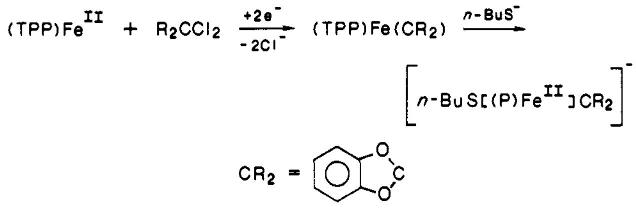
Cytochrome P-450 iron–carbene complexes are formed during oxidative metabolism of 1,3-benzodioxole derivatives, which are used as insecticide synergists (Scheme 4).[42]

A model compound of this cytochrome P-450 complex has been prepared.[42] Addition of excess *n*-butylthiolate to the $(TPP)Fe^{II}$(1,3-benzodioxol-2-ylidene) complex leads to the expected (TPP)Fe(1,3-benzodioxol-2-ylidene)(*n*-BuS⁻) as shown in Scheme 5.

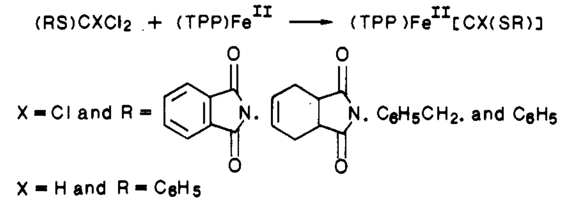
Reaction of (trichloromethyl)thioalkyl compounds with iron(II) porphyrins in the presence of excess reducing agent also leads to the formation of $(P)Fe^{II}$(CCl(SR)) carbene complexes (Scheme 6).

The $(P)Fe^{II}$(CCl(SR)) derivatives provide a new synthetic route to thiocarbonyl iron complexes since some of them are decomposed into (P)Fe(CS) upon treatment with catalytic amounts of $FeCl_2$ or $CuCl_2$.[43] $(TPP)Fe(CH(SC_6H_5))$ provides the first example of an iron(II) porphyrin complex bearing a secondary CHR carbene. Also, reduction of $CF_3CHClBr$ by $(TPP)Fe^{II}$ in the presence of sodium dithionite leads to a σ-bonded iron–alkyl complex, $(TPP)Fe^{III}(CHClCF_3)$, whereas reduction of the CF_3CCl_3 analogue under the same experimental conditions gives the expected $(TPP)Fe^{II}(CClCF_3)$ carbene complex.[12]

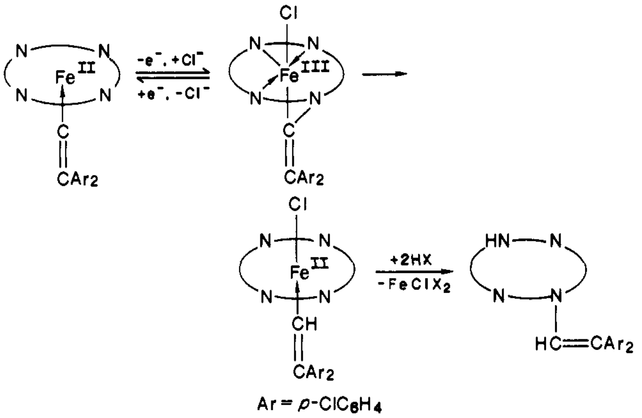
SCHEME 5



SCHEME 6



SCHEME 7



The reactivity of iron porphyrin carbenes toward primary amines has been used to synthesize isonitrile complexes[12,44,45] (eq 13).

$$(P)Fe^{II}CCl_2 \underset{-RNH_2}{\overset{RNH_2}{\rightleftharpoons}} (P)Fe^{II}(CCl_2)(RNH_2) \rightarrow (P)Fe^{II}(RNC)(RNH_2) \tag{13}$$

The iron porphyrin–vinylidene complexes lead to N-substituted porphyrins according to Scheme 7, where Ar = $p\text{-}ClC_6H_4$.[46]

N-Substituted porphyrins are formed in high yields upon the addition of CF_3COOH or $FeCl_3$ to the singly oxidized iron porphyrin–vinylidene carbene complexes.[46] The first one-electron oxidation step of the starting $(P)Fe^{II}(CCAr_2)$ complex is reversible and leads to a complex possessing a bridged carbene between the iron atom and one nitrogen atom.

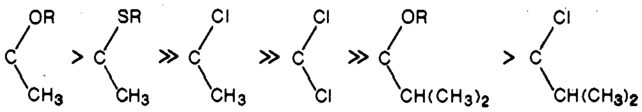
Two independent groups have determined the crystal structure of similar complexes.[47,48] The large Fe–N distance of 2.52 Å for $(TPP)Fe^{III}[C{=}C(p\text{-}ClC_6H_4)_2]Cl$[47] indicates that the metal is five-coordinated and that the iron is not linked to one of the four pyrrole nitrogens. This produces a highly distorted coordination polyhedron of the iron atom and results in a stable intermediate-spin-state ($S = {}^3/_2$) complex both in solution and in the solid state.[49]

Structural parameters of $(TPP)Fe(CCl_2)(H_2O)$[34] and other models were used to calculate an energy level diagram for the valence orbitals.[50] This study demonstrated how the addition of an axial ligand leads to the specific structures given in ref 47 and 48. The calculations suggest that a bridging structure should result from electrophilic attack of a pyrrole nitrogen on the vinylidene carbon. Indeed, the calculated charge on the vinylidene carbon of $(TPP)Fe(C{=}CAr_2)$ is negative, which contrasts with the large positive charge on the corresponding carbon of $(TPP)Fe(CCl_2)$. Thus, a bridging iron–dichlorocarbene cannot occur for $(TPP)Fe(CCl_2)$. To date, this theoretical study is in good agreement with known experimental data.

The α-halocarbene–porphyrin complexes, (P)Fe(CCl(R)), react with alcohols or thiols to give (P)Fe(CR(OR′)) or (P)Fe(CR(SR′)) derivatives.[51] These reactions are summarized in eq 14, where XR′ and R =

$$(P)Fe^{II} + RCCl_3 \xrightarrow[CH_2Cl_2,\ R'XH,\ -HCl]{Fe,\ -2Cl^-} (P)Fe(CR(XR')) \qquad (14)$$

OCH_3 and CH_3; OC_2H_5 and CH_3; $SCH_2C_6H_5$ and CH_3; or OCH_3 and $CH(CH_3)_2$. This study also leads to the following decreasing order of reactivity for the carbene complexes:[51]



C. Electrochemistry of σ-Bonded Iron–Alkyl and Iron–Aryl Porphyrins

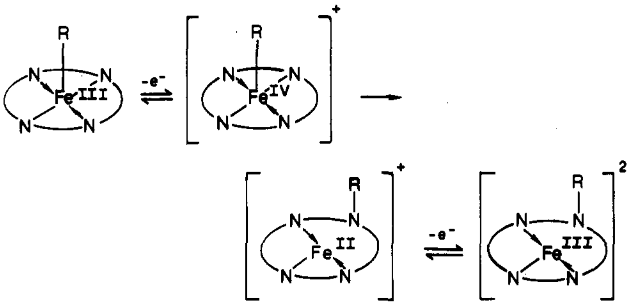
The electrochemistry of σ-bonded iron porphyrins has been carried out almost exclusively by the groups of Lexa and Savéant[16,17] and Kadish and Guilard.[15,29,52,53]

Studies of (P)Fe(R) oxidation can be divided into two groups of complexes that vary according to the reactivity of the singly oxidized species. The first group comprises metalloporphyrins where a rapid migration of the σ-bonded ligand on $[(P)Fe(R)]^+$ leads to an N-alkyl or N-aryl derivative. This group is typified by $(OEP)Fe(C_6H_5)$ and $(TPP)Fe(C_6H_5)$.[29] The second group of metalloporphyrins comprises those in which the migration does not occur or is too slow to be observed. This group is typified by $(P)Fe(C_6F_5)$,[15] $(P)Fe(C_6F_4H)$,[15] and $(P)Fe(CH_3)$.[53] No migration is observed on the electrochemical time scale, and these complexes undergo well-defined reversible one-electron oxidations. A description of the migration reaction and the properties of stable oxidized and reduced σ-bonded iron porphyrins is given in the following sections.

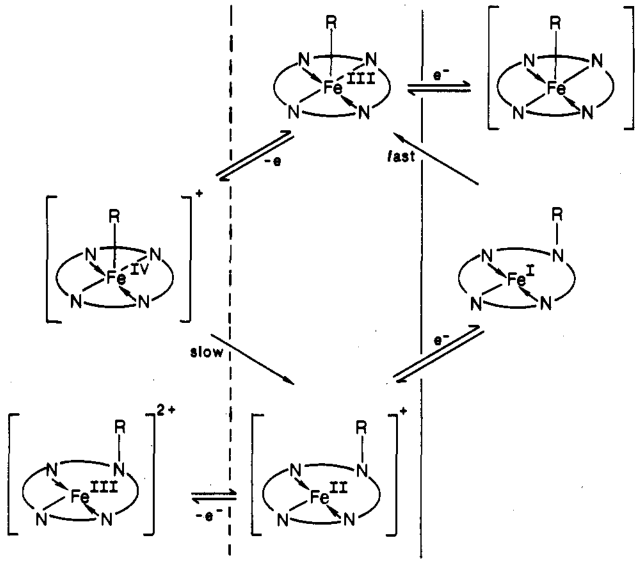
D. Electrochemically Initiated Migration of Aryl Groups

The two-electron electrooxidation of $(TPP)Fe(C_6H_5)$ or $(OEP)Fe(C_6H_5)$ proceeds via an initial reversible one-electron abstraction to yield $[(TPP)Fe(C_6H_5)]^+$ or $[(OEP)Fe(C_6H_5)]^+$. These singly oxidized complexes are not stable and undergo a series of chemical and electrochemical reactions that ultimately lead to the iron(III)-N-phenyl porphyrins $[(N\text{-}C_6H_5TPP)Fe^{III}]^{2+}$ or $[(N\text{-}C_6H_5OEP)Fe^{III}]^{2+}$. Both derivatives can be reversibly reduced by a single electron to quantitatively give $[(N\text{-}C_6H_5TPP)Fe^{II}]^+$ or $[(N\text{-}C_6H_5OEP)Fe^{II}]^+$. Further reductions are also possible and give a transient species tentatively identified as an N-phenyl iron(I) porphyrin.[29]

SCHEME 8



SCHEME 9



The overall two-electron oxidation of $(P)Fe(C_6H_5)$ involves a chemical reaction coupled between two reversible electrochemical reactions (an electrochemical ECE type mechanism) as shown in Scheme 8 where R = C_6H_5.

$[(OEP)Fe(C_6H_5)]^+$ has no significant electronic absorption bands between 600 and 900 nm, and values of molar extinction coefficients for this complex are very close to the corresponding values of the neutral species. In addition, there is a sharp blue-shifted β band in the spectrum. This type of spectrum is not characteristic of a porphyrin cation radical, and, on this basis, the oxidized species was characterized as containing Fe(IV).[29] A similar assignment of Fe(IV) was also obtained by Balch and Renner[30] for chemically in situ generated $[(TMP)Fe(C_6H_4X)]^+$ where X = CH_3 or H. ^1H NMR data were used to assign the Fe(IV) oxidation state.

The reduction of electrogenerated $[(N\text{-}C_6H_5P)Fe^{II}]^+$ was also found to proceed via an ECE mechanism in which the chemical step was a migration of the phenyl group from the nitrogen of the porphyrin ring to the central iron atom, thus regenerating the initial σ-bonded complex.[29] This overall oxidation/reduction sequence involving a "reversible" migration of the phenyl group is shown in Scheme 9, where R = C_6H_5.

A similar reversible migration of $CH{=}C(C_6H_5)_2$, C_6H_5, and CH_3 from (TPP)Fe(R) was reported by

Mansuy[27] using $FeCl_3$ as a chemical oxidizing agent and $[S_2O_4]^{2-}$ as a chemical reducing agent. On the basis of these studies it was thought that a similar migration sequence would occur for a large number of σ-bonded alkyl and aryl groups on (P)Fe(R). This does not, however, seem to be the case.

The conversion of (P)Fe(R) to $[(N\text{-RP})Fe]^+$ occurs when R = C_6H_5,[27,29,30] p-$CH_3C_6H_4$,[30] or m-$CH_3C_6H_4$[30] but not when R = C_6F_5[15] or C_6F_4H.[15] The iron(III) in $(P)Fe(C_6F_5)$ and $(P)Fe(C_6F_4H)$ are in the high-spin state[15] while iron(III) in $(P)Fe(C_6H_5)$ is in the low-spin state at room temperature. This difference in spin state between the phenyl-substituted and the perfluoroaryl-substituted complexes might be one factor related to the lack of (or slow) migration involving the σ-bonded perfluoroaryl porphyrins. However, $(P)Fe(CH_3)$ is also low spin at room temperature,[21] and an electrochemically initiated migration does not occur for these compounds on the cyclic voltammetric time scale.[53]

It is possible that differences in the donor properties of the ligand may influence the migration step of $[(P)Fe(R)]^+$. However, insufficient information has been published on this subject. In this regard, it should be noted that metal-to-nitrogen migrations have been reported for σ-bonded (P)Co(R) complexes where R = CH_3,[54] C_2H_5,[55] $CO_2C_2H_5$,[55] or C_6H_4X[56] (X = OCH_3, CH_3, Br, Cl, or H). However, the reactions of σ-bonded cobalt porphyrin species differ from those of σ-bonded iron species in that the initial oxidation of (P)Co(R) proceeds via a cation radical[56] rather than via an oxidized metal atom.

Metal-to-nitrogen migrations have also been reported for iridium[57] (R = CH_3) and rhodium porphyrins[58-60] (R = CH_3 or C_2H_5) but none of these reactions have been observed to occur via electrochemical initiation. It thus appears that the σ-bonded iron and cobalt porphyrins are unique in the fact that they undergo a migration reaction that is electrochemically initiated.

E. Reversible Electrode Reactions of (P)Fe(R)

Reversible potentials for oxidation and reduction of (P)Fe(R) may be obtained in the absence of a migration step. In these cases, dramatic cathodic shifts of half-wave potentials are observed for both oxidation and reduction of the (P)Fe(R) complexes with respect to the corresponding (P)FeX derivatives (where X is an anionic ligand) in the same media.[15,29] For example, the first reduction and first oxidation of $(TPP)Fe(C_6H_5)$ and $(OEP)Fe(C_6H_5)$ are shifted by up to 800 mV with respect to the first reduction and first oxidation of $(TPP)FeClO_4$.[61] Each electrode reaction of $(TPP)Fe(C_6H_5)$ and $(OEP)Fe(C_6H_5)$ is reversible to quasi-reversible on the cyclic voltammetric time scale, but, as mentioned above, a migration of the phenyl group of $(P)Fe(C_6H_5)$ occurs on longer time scales.

Half-wave potentials for the reversible oxidation or reduction of (P)Fe(R) are directly influenced by the electron donor or electron-withdrawing groups on the porphyrin ring. This was initially pointed out by Laviron and Guilard[10] for the reactions of $(OEP)Fe(CH_3)$ and $(TPP)Fe(CH_3)$ and by Lexa and Savéant[16,17] for the reactions of (P)Fe(R) where P was $C_{12}TPP$, OEP, DP, or TPP and R was one of several different alkyl groups. For a given R group (such as CH_3) the $E_{1/2}$ values became progressively more negative as the macrocycle basicity increased and followed the order TPP < $C_{12}TPP$ < DP < OEP.[16]

It was originally suggested that there was very little dependence of the R group on reduction potentials of (P)Fe(R).[16] This is true for (P)Fe(R) where R is a simple alkyl group but not for complexes where R is an aryl group such as C_6H_5, C_6F_5, or C_6F_4H. Replacing either four or five of the protons on C_6H_5 by fluoro atoms contributes to a 70–80-mV positive shift of the half-wave potential for each F atom. A similar positive potential shift is observed upon adding electron-withdrawing CN groups to the TPP of $(TPP)Fe(C_6H_5)$.[15] For example, the difference between $(P)Fe(C_6H_5)$ reduction where P = $(CN)_4TPP$ and P = TPP is 670 mV, with the former complex being the most easy to reduce ($E_{1/2}$ = −0.03 V in PhCN, 0.1 M $TBA(PF_6)$).

The neutral (P)Fe(R) complex contains a formal Fe(III) oxidation state and after reduction by one electron leads to a complex having a formal Fe(II) oxidation state. The electrogenerated $[(TPP)Fe(C_6H_5)]^-$ and $[(OEP)Fe(C_6H_5)]^-$ complexes have optical absorption spectra with a Soret region characteristic of an Fe(II) porphyrin.[29] On the other hand, the electronic absorption spectra of $[(OEP)Fe(C_6H_5)]^-$ and $[(TPP)Fe(C_6H_5)]^-$ also have absorption maxima close to 760 nm, which is uncharacteristic of synthetic Fe(II) porphyrins. However, similar absorption bands are found for a number of porphyrin anion radicals[62] as well as for oxyheme complexes.[63]

Because $[(P)Fe(C_6H_5)]^-$ has spectral properties of both Fe(II) and an Fe(III) anion radical, the resonance hybrid shown in eq 15 was suggested.[29]

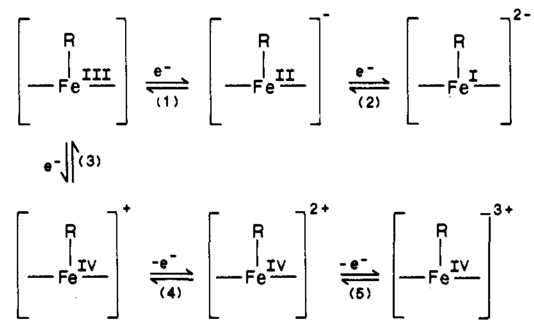
$$[(P)Fe^{II}(C_6H_5)]^- \leftrightarrow [(P)Fe^{III}(C_6H_5)]^{\bullet -} \quad (15)$$

Oxidized six-coordinate σ-bonded complexes have only been reported as transient intermediates.[52] However, formation of neutral $(P)Fe(C_6H_5)(L)$ from $(P)Fe(C_6H_5)$ has been monitored both spectrally[30,52] and electrochemically.[52] Formation constants of $10^{1.6}$ to $10^{2.5}$ were calculated for pyridine binding by the five-coordinate σ-bonded Fe(III) complexes.[52] In addition, the six-coordinate $(P)Fe(C_6H_5)(L)$ adducts where L = imidazole[20] or py[52] were characterized by ^1H NMR studies.

The reduction of $(P)Fe(C_6H_5)(py)$ is electrochemically reversible, and stable solution products have been spectroscopically identified.[52] Potentials for the reduction are shifted in a negative direction from those of $(P)Fe(C_6H_5)$, consistent with stabilization of the six-coordinate species. The reduction of $(P)Fe(C_6H_5)(py)$ has also been proposed to yield a resonance hybrid involving an Fe(II) complex and an Fe(III) anion radical.[52] This is similar to the assignment for $[(P)Fe(C_6H_5)]^-$ (see eq 15) but UV-vis data of the six-coordinate $(P)Fe(C_6H_5)(py)$ complexes indicate a smaller contribution of the anion radical form to the resonance hybrid.

Scheme 10 outlines the possible (simplified) electron-transfer reactions that may occur for σ-bonded iron–alkyl or iron–aryl porphyrins in noncoordinating media. Reactions 1, 3, and 4 in Scheme 10 have been observed for $(TPP)Fe(C_6H_5)$ and $(OEP)Fe(C_6H_5)$[29] while reaction 2 has been limited to the more easily reducible $((CN)_4TPP)Fe(C_6H_5)$[15] and $(T(pCF_3)PP)Fe(C_6H_5)$[53] complexes. Reaction 5 corresponds to a generation of an Fe(IV) dication and has yet to be experimentally observed. However, this reaction should be

SCHEME 10



accessible within the potential range of many electrochemical solvents and may occur for porphyrins that contain electron donor groups on the macrocycle. Spin-state changes for (P)Fe(R) (see Scheme 1) and chemical reactions involving $[(P)Fe(R)]^+$ (see Scheme 9) are not included in Scheme 10. Also, the central Fe(II), Fe(III), Fe(IV), and formally Fe(I) atoms may lie in or out of the porphyrin plane, depending upon the nature of the porphyrin ring and the R group. This is also not illustrated in the schematic representation.

Scheme 10 indicates that up to five electron transfers are possible for a given (P)Fe(R) complex but the actual observed number of electrode reactions for a given σ-bonded iron porphyrin will vary as a function of the porphyrin ring basicity and the specific R ligand on (P)Fe(R). In addition, bonding of a solvent molecule or a nitrogenous base to the central metal ion of neutral, oxidized, or reduced (P)Fe(R) will significantly increase the number of possible electron transfers. This is shown in Scheme 11, which illustrates some of the possible electron-transfer pathways for reduction or oxidation of various (P)Fe(R) and (P)Fe(R)(L) complexes.

In summary, the exact nature of the electron transfers involving (P)Fe(R) or (P)Fe(R)(L) and the stability of the electrogenerated high- or low-valent iron species will depend upon the donicity of the R group, the basicity of the porphyrin ring, and the nature of any sixth axial ligand.

F. Electrochemistry of Iron–*N*-Alkyl and Iron–*N*-Aryl Porphyrins

Biological implications of *N*-alkyl porphyrins[26,28,64-68] have generated a renewed interest in understanding the chemical behavior and physicochemical properties of these complexes.

The synthesis of free-base *N*-alkyl porphyrins is rather difficult, and studies of iron–*N*-alkyl porphyrins were initially limited to the *N*-methyl derivatives.[69-71] More recently, the synthesis of $N\text{-CH=C}(p\text{-}C_6H_4Cl)_2$, $N\text{-CH=C}(p\text{-}C_6D_4Cl)_2$, $N\text{-CH=C}(p\text{-}C_6H_4Cl)_2$, and $N\text{-}C_6H_5$ chloroiron(II) derivatives were reported.[72,73] In addition, the $(N\text{-RTPP})Fe^{II}Cl$ derivatives (where R = $CHC(C_6H_5)_2$, C_6H_5, and CH_3) have been synthesized by oxidative migration of the R group from iron to nitrogen in (P)Fe(R)[27] (see Scheme 2). Additional novel *N*-aryl porphyrins can also be synthesized by the electrochemical oxidation of σ-bonded Fe(III) porphyrins. This reaction is given by Scheme 12 and was first demonstrated for the case of $(P)Fe(C_6H_5)$.[29]

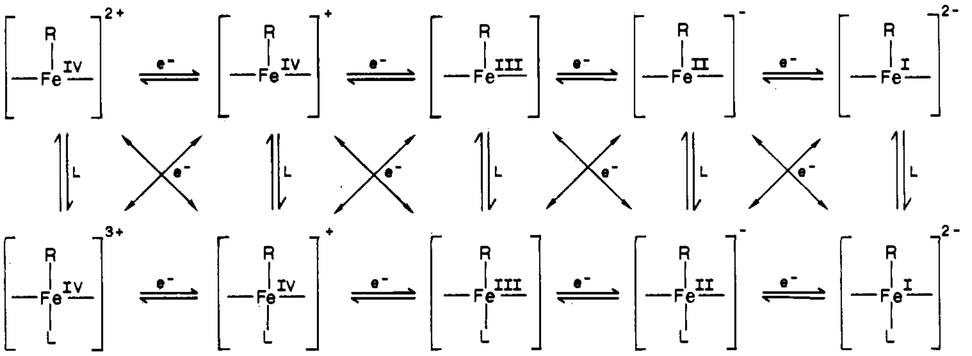
The *N*-alkyl and *N*-aryl species exist as air-stable complexes and have an associated anion coordinated to the iron(II).[69,70] The Fe(II)/Fe(III) oxidation of $(N\text{-}CH_3TPP)FeCl$ occurs at 0.50 V in CH_2Cl_2,[72] and this potential is close to the potentials of 0.44 and 0.54 V for oxidation of $(N\text{-}C_6H_5TPP)FeCl$ in PhCN[29] and DMF,[72] respectively. These values may be compared to a half-wave potential of −0.06 V for oxidation of $(N\text{-}C_6H_5TPP)FeClO_4$ in PhCN. The 600-mV potential difference between $E_{1/2}$ values for $(N\text{-}C_6H_5TPP)FeClO_4$ and $(N\text{-}C_6H_5TPP)FeCl$ oxidation may be due to an increased stabilization of Fe(II) by the chloride anion.

Additional oxidations of *N*-alkyl and *N*-aryl porphyrins are also possible, but these reactions have only been reported for $[(N\text{-}CH_3TPP)FeCl]^+$, which is oxidized at 1.52 V vs SCE.[72] This reaction was assigned as an oxidation at the porphyrin π ring system[72] and was made by comparing the electrochemistry of $(N\text{-}CH_3TPP)ZnCl$ with that of $(N\text{-}CH_3TPP)FeCl$. However, in the absence of spectral data, the electrogeneration of an Fe(IV) N-substituted porphyrin cannot be ruled out.

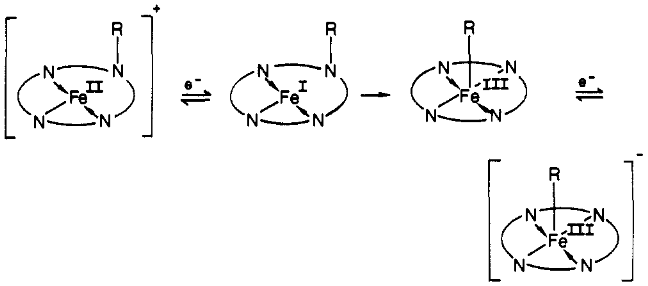
Electrochemical studies of chemically synthesized N-substituted porphyrins are limited to $(N\text{-}C_6H_5TPP)FeCl$, $(N\text{-}CH_3TPP)FeCl$, and $(N\text{-}C_2H_5TPP)FeCl$.[72] The latter two complexes undergo two reversible reductions.[72] No detectable migration of the alkyl group was reported, but this may occur at longer time scales and in very small yields which are not detected electrochemically. The first reductions of (*N*-RTPP)FeCl where R = C_6H_5, CH_3, or C_2H_5 were tentatively assigned as an Fe(II)/Fe(I) transition[29,72] while the second reduction was assigned as a reaction at the porphyrin π ring system.[72] However, to date, no spectral identification has been provided to confirm the oxidation state of any *N*-alkyl porphyrin reduction products.

Iron(III)–*N*-alkyl porphyrins can form monoadducts with nitrogenous bases,[71,73] and a number of different electron-transfer pathways are possible depending upon the nature of the sixth axial ligand. In addition, the

SCHEME 11



SCHEME 12



electrochemistry of (N-C_6H_5TPP)$Fe^{II}ClO_4$ in pyridine has been reported[52] and is similar to that which is observed in PhCN.[29]

G. Electrochemistry of Spin Equilibria and Spin Mixture Systems

The type and number of axial ligands bound to the iron atom of (P)FeX, (P)FeX(L), or $[(P)Fe(L)_2]^+X^-$ are two major factors that influence the spin state of the central iron atom.[74,75] A variation of the axial and macrocyclic ligands on (P)Fe(R) or (P)Fe(R)(L) can also affect the magnetic properties of the σ-bonded complex.[15,21]

The exact spin state of Fe(III) in (P)Fe(R) will depend on the nature of the alkyl or aryl group, the nature of the equatorial ligand, and the temperature. The formation of complexes with σ-bonded iron species seems to play a fundamental role in the biological activity of cytochrome P-450,[28,36,76–78] and, therefore, it is important to understand the molecular parameters that determine a given spin state.

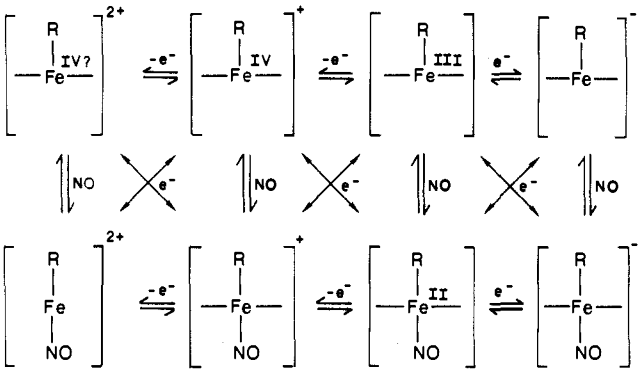
There may be a direct correlation between the spin state of Fe(III) in (P)Fe(R) and the stability of the oxidized $[(P)Fe(R)]^+$ or reduced $[(P)Fe(R)]^-$ species, but further studies are needed to verify this. For example, the high-spin σ-bonded perfluoro complexes are unstable after a one-electron reduction but are moderately stable upon being oxidized by one electron.[15] In contrast, singly reduced, low-spin, σ-bonded C_6H_5 complexes are extremely stable but the singly oxidized complexes undergo a rapid migration of the phenyl group.[29]

H. Electrochemistry of Iron–Alkyl and Iron–Aryl Porphyrins Containing Bound Diatomic Molecules

It is well established that diatomic π-acceptor ligands such as CO,[79–81] NO,[82–84] CS,[85–88] or CSe[89] strongly coordinate to Fe(II) porphyrins and that these complexes may be oxidized in nonbonding media to yield Fe(III) complexes where NO, CS, and CSe (but not CO) are also coordinated.[86–93]

A coordination of NO by σ-bonded alkyl or aryl iron(III) porphyrins is also possible. Six-coordinate OEP and TPP nitrosyl porphyrin complexes with σ-bonded CH_3, n-C_4H_9, C_6H_5, p-$CH_3C_6H_4$, p-$OCH_3C_6H_4$, or C_6F_4H groups were characterized by ^1H NMR, IR, and UV–visible spectroscopy.[94,95] On the basis of these data the central metal of (P)Fe(R)(NO) was assigned as being in the Fe(II) oxidation state.[94,95] Electrochemical studies show that $[(P)Fe(C_6H_5)(NO)]^+$ is obtained upon oxidation of $(P)Fe(C_6H_5)(NO)$.[94] This reversible oxidation occurs at potentials shifted positively with respect to those of (P)Fe(R), (P)Fe(R)(py), and (P)Fe(NO).[61] For example, $(TPP)Fe(C_6H_5)$ is oxidized at 0.61 V in PhCN while $(TPP)Fe(C_6H_5)(py)$ has an oxidation potential of 0.53 V in PhCN containing 1 M pyridine. In the same solvent system (TPP)Fe(NO) is reversibly oxidized at 0.75 V and $(TPP)Fe(C_6H_5)(NO)$ is reversibly oxidized at 0.86 V under a partial NO pressure of 72 mmHg. This formal Fe(II)/Fe(III) potential is shifted by over 1.5 V from the formal Fe(II)/Fe(III) potential of $(TPP)Fe(C_6H_5)$ and is consistent with the strong stabilization of an Fe(II) oxidation state by NO, even in the presence of a σ-bonded phenyl group.

SCHEME 13



A summary of the possible electrode reactions of (P)Fe(R) and (P)Fe(R)(NO) in nonaqueous media is shown in Scheme 13. It is known that the starting oxidation state of the iron in (P)Fe(R)(NO) is +2, but no information has been published with respect to characterizing the site of electron abstraction from or electron addition to (P)Fe(R)(NO) (i.e., reaction at the central metal, NO ligand, or π ring system). It is also not known how the reactions in Scheme 13 will vary as one changes the nature of the R group or the porphyrin π ring system.

IV. Ruthenium, Osmium, and Molybdenum

Neutral, reduced, and oxidized ruthenium porphyrin dimers can be used in the preparation of monomeric σ-bonded, carbene, or π complexes.[96–100] These are the only examples where a metalloporphyrin containing the same central metal has been shown to exhibit all three types of metal–carbon bonds.

The reaction of reduced ruthenium and osmium porphyrin dimers of the form $[(P)M]^{2-}$ with alkyl iodide to produce dialkyl complexes occurs according to eq 16, where M = Ru or Os and RX = CH_3I or C_2H_5I.[96–98]

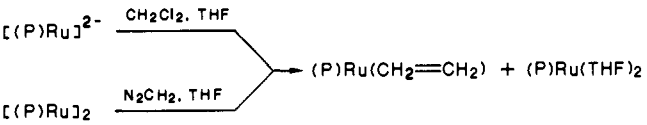
$$[(P)M]^{2-} + 2RX \rightarrow (P)M(R)_2 + 2X^- \qquad (16)$$

The resulting six-coordinate d^4 dialkyl derivatives $(P)M(R)_2$ are diamagnetic and the $(P)Ru(C_2H_5)_2$ complexes decompose, giving rise to $(P)Ru(CH(CH_3))$. A later mechanistic study[97] demonstrated that such a conversion occurs via a radical process. The first step of the reaction (eq 17) involves reversible homolysis of

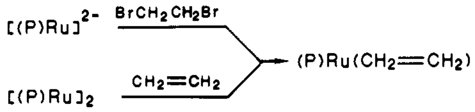
$$(P)Ru(C_2H_5)_2 \rightleftarrows (P)Ru(C_2H_5) + {}^\bullet C_2H_5 \qquad (17)$$

the ruthenium–carbon bond and leads to the paramagnetic σ-bonded $(P)Ru(C_2H_5)$ species and an ethyl radical. The generated ethyl radical can abstract a hydrogen atom from one axial ligand of $(P)Ru(C_2H_5)_2$,

SCHEME 14



SCHEME 15



giving rise to an ethylidene species. Addition of excess radical trap then permits the clean preparation of (P)Ru(C_2H_5).

Other six-coordinate Ru(IV) complexes of the type (P)Ru$(R)_2$ where R is an aryl or an alkyl group have been prepared and characterized by James and Dolphin.[99] The thermal decomposition of these products leads to formation of five-coordinate Ru(III) species of the type (P)Ru(R). A number of these five-coordinate complexes have been prepared and were characterized by ^{1}H NMR spectroscopy.[100] One of the complexes, (OEP)Ru(C_6H_5), was structurally characterized and has a ruthenium–carbon bond distance of 2.005 Å.

Carbene complexes of ruthenium are formed from the reaction of neutral $[(P)Ru]_2$ dimers with diazoalkanes. This reaction is given by eq 18, where R = CH_3 or $CO_2CH_2CH_3$. Reaction of the $[(P)Ru]^{2-}$ dianion with

$$[(P)Ru]_2 \xrightarrow{+N_2CHR} (P)Ru(CH(R)) \qquad (18)$$

gem-dihalides also leads to carbene complexes of the type (P)Ru(CH(R)) where R = CH_3 or $Si(CH_3)_3$ as well as (P)Ru(C═CR_2) where R = *p*-C_6H_4Cl.

$$[(P)Ru]^{2-} \xrightarrow{Cl_2CR_2} (P)Ru(CR_2) \qquad (19)$$

(TPP)Ru(C═C(*p*-$C_6H_4Cl)_2$) had previously been synthesized by metalation of a free-base porphyrin containing the carbene unit which is bridged between two pyrrole nitrogen atoms.[101]

Surprisingly, the reaction of $[(P)Ru]^{2-}$ with methylene chloride in THF gives a mixture of the (P)Ru(CH_2═CH_2) π complex and (P)Ru$(THF)_2$. The same products are formed when $[(P)Ru]_2$ reacts with N_2CH_2 (Scheme 14). It has also been suggested[98] that the reactions in Scheme 14 might involve a (P)Ru(CH_2) carbene intermediate.

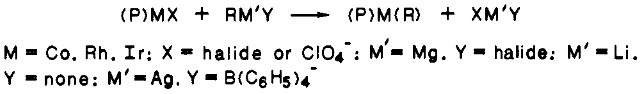
Treatment of $[(P)Ru]_2$ with ethylene in THF yields (P)Ru(CH_2═CH_2). This π complex is also obtained by the reaction of $[(P)Ru]^{2-}$ with 1,2-dibromoethane (Scheme 15), and the analogous osmium complex, [(P)Os(CH_2═CH_2)], has been isolated according to the same procedure.[98] The only previously reported porphyrin π complex was (TPP)Mo(PhC≡CPh).[102]

V. Cobalt, Rhodium, and Iridium

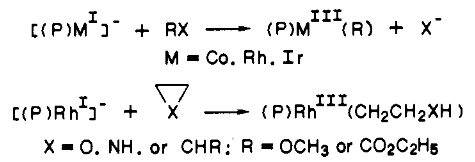
A. Synthesis and Reactivity

Three types of metal–carbon complexes have been reported for cobalt, rhodium, and iridium porphyrins. The first contains a single metal–carbon σ bond and includes Co, Rh, and Ir porphyrins. The second type of metal–carbon complexes contains a carbene fragment that is inserted between the metal–nitrogen bond. Such a species has only been reported for cobalt porphyrins. The third type of metal–carbon complexes is that which has a π bond. In the cobalt triad, these have only been postulated for Rh porphyrins.

SCHEME 16



SCHEME 17



The reaction of (P)M(X)(L) with Grignard reagents or with alkyl- or aryllithium gives the corresponding monoalkyl or monoaryl complexes and has been used for preparation of σ-bonded cobalt,[7,55,56,103,104] rhodium,[60,105–115] and iridium[116,117] alkyl or aryl complexes (Scheme 16).

The two-electron oxidative addition of alkyl or aryl halides or cyclopropane derivatives to $[(P)M^I]^-$ also leads to Co(III),[7,55,118–123] Rh(III),[59,60,112,124–127] and Ir(III)[116,117,128] alkyl or aryl porphyrins. This reaction is shown in Scheme 17 and is similar to the synthetic route used to obtain σ-bonded iron–alkyl porphyrins.

Alkyl cobalt(III) porphyrins have been prepared in good yields from $[(P)Co^I]^-$ but aryl cobalt(III) porphyrins are best synthesized by reacting (P)CoCl or (P)Co(Cl)(py) with either aryllithium or Grignard reagents.[103]

Oxidative addition of RX to Rh(I) porphyrins also produces σ-bonded complexes (eq 20). Organic substrates include anhydrides,[129] amides,[130] strained carbocycles,[131] and ketones.[126]

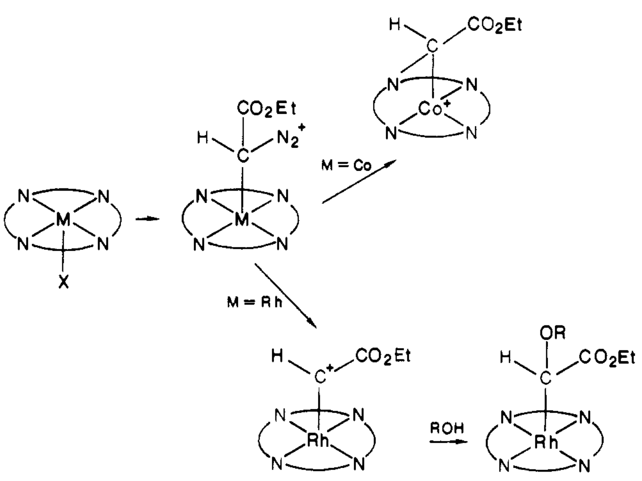
$$(P)[Rh^I(CO)_2]_2 + RX \rightarrow (P)Rh(R) + [Rh^I(CO)_2]^+ + X^- + 2CO \qquad (20)$$

The reaction of ionic cobalt(III)[132–134] and ionic rhodium(III) porphyrins[135,136] with diazoalkanes has been described by Callot and co-workers. Various carbene bonded complexes such as (P)M(═CRR′) are formed, where R or R′ = H, CH_3, or an alkyl carboxylate group. The first step of this reaction is given by eq 21 for (P)RhX and (P)CoX. Several significant differences

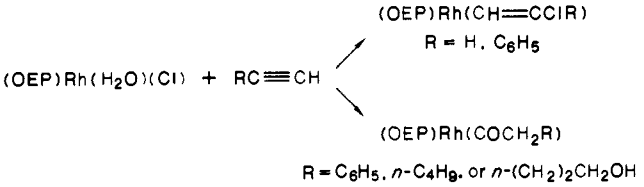
$$(P)MX + N_2C(R)(R'{-}H) \rightarrow (P)M({=}CRR') + N_2 + HX \qquad (21)$$

exist between the reactivities of cobalt(III) and rhodium(III) porphyrins toward diazoalkanes. Alkyl metal(III) porphyrins are easily isolated in the Rh and Co series. However, a catalytic decomposition of excess diazoalkane occurs in the Rh series. This evolution induces carbene transfer to various substrates. Ethyl diazoacetate possesses typical behavior since a stable inserted cobalt complex results from insertion of the carbene fragment between nitrogen and cobalt. In contrast, the reaction of ethyl diazoacetate with rhodium porphyrins leads to different final products[136] as shown in Scheme 18 but the loss of N_2 does not involve the participation of a pyrrolic nitrogen.

SCHEME 18



SCHEME 19



Differences between the reactions in Scheme 18 in the rhodium and cobalt series can be explained by the greater stability of the rhodium–nitrogen bond.[137] The stability of the d^6 cobalt(III)–carbene complexes in $[(OEP)Co(CHCO_2Et)]^+Cl^-$ [138,139] and $[(TPP)Co(CHCO_2Et)]^+Cl^-$ [140] has also been discussed in a theoretical study.[50] Calculations demonstrate that the stability of an inserted carbene complex relative to that of the monocoordinate carbene is increased upon going from a d^6 to a d^8 complex.

Specific procedures have been published for synthesizing σ-bonded rhodium porphyrins. Nucleophilic attack of the CO ligand by an ethoxy anion leads to an ethyl carboxylate rhodium(III) complex[141] as shown in eq 22. $(OEP)Rh(H_2O)(Cl)$ reacts with ethyl vinyl ether

$$(P)Rh(CO)Cl + EtO^- \rightarrow (P)Rh(CO_2Et) + Cl^- \qquad (22)$$

in the presence of ethanol to give a rhodium(III) porphyrin that is readily hydrolyzed to produce $(OEP)Rh(CH_2CHO)$ (eq 23). The same complex can react

$$(OEP)Rh(H_2O)(Cl) + CH_2{=}CHOEt \xrightarrow{EtOH} (OEP)Rh(CH_2CH(OEt)_2) \xrightarrow{H_3O^+} (OEP)Rh(CH_2CHO) \qquad (23)$$

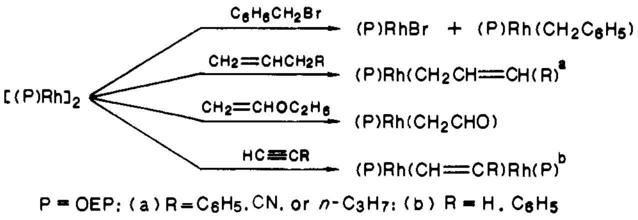
with acetylenic compounds, and various derivatives such as vinyl or acyl rhodium(III) porphyrins can be obtained[117] (Scheme 19).

Wayland first reported the preparation of a metalloformyl porphyrin complex by the insertion of CO between the rhodium–hydride bond of (OEP)RhH[108] (eq 24). Halpern[142] demonstrated that the radical

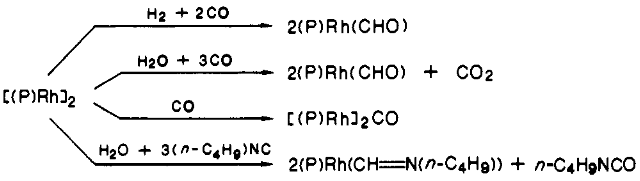
$$(OEP)RhH + CO \rightarrow (OEP)Rh(CHO) \qquad (24)$$

mechanism of this process was initiated by an equilibrium between the (OEP)RhH hydride and the $[(OEP)Rh]_2$ dimer. Homolytic dissociation of $[(P)Rh]_2$ gives rise to the •Rh(OEP) radical, which induces the radical chain process.

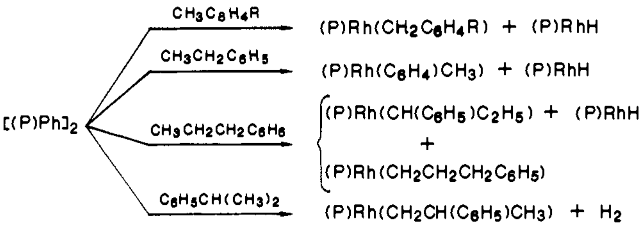
SCHEME 20



SCHEME 21



SCHEME 22



Attempts to insert CO between the Ir–H bond of (OEP)IrH have been unsuccessful.[143] Thermodynamic studies of Rh–H and Ir–H insertion reactions demonstrate that differences between the M–H and M–C bond energies and the acceptor properties of the five-coordinate hydride species lead to unfavorable conditions for producing (OEP)Ir(CHO).

Ogoshi[144] and Wayland[145–152] demonstrated the fascinating synthetic ability of dimeric rhodium porphyrins for preparing metal–carbon bonded derivatives. The reaction of $[(OEP)Rh]_2$ with alkyl halides, unactivated olefins, or acetylene produces σ-bonded (P)Rh(R) complexes[144] (Scheme 20).

Reactions of $[(P)Rh]_2$ with carbon monoxide and alkyl isocyanides have also been investigated.[147] An alternative preparation of the (P)Rh(CHO) metalloformyl complex involves the water gas shift reaction with $[(P)Rh]_2$. This reaction is thought to occur via the hydrogen source in a transient (P)RhH species. Isocyanides have a similar but enhanced reactivity compared to carbon monoxide (Scheme 21).

$[(P)Rh]_2$ reacts thermally with toluene and methyl-substituted aromatics at the methyl C–H bond to form (P)Rh(R), where R = $CH_2C_6H_4R'$ (R′ = H, *p*-CH_3, or *m*-CH_3), $CH(C_6H_4)CH_3$, $CH(C_6H_5)C_2H_5$, or $CH_2CH(C_6H_5)(CH_3)$.[150] Formation of (P)RhH induces elimination of a hydrogen atom (see Scheme 22). The initial attack of long-chain substituents involves the benzylic C–H bond, and a subsequent rearrangement gives rise to the less hindered σ-bonded alkyl species. The formation of $(P)Rh(CH_2CH(C_6H_5)CH_3)$ from $[(P)Rh]_2$ is only observed with $C_6H_5CH(CH_3)_2$, whereas the reaction of $[(P)Rh]_2$ with $CH_3CH_2CH_2C_6H_5$ leads to two complexes (Scheme 22).

$[(P)Rh]_2$ reacts with α-CH bonds and aldehydic CH bonds of aldehydes and ketones such as $CHR^1R^2C(O)R^3$, where R^1 and R^2 = H or CH_3 and R^3 = H, CH_3, or C_6H_5.[152] This leads to (P)RhH and metallo β-carbonyl compounds such as $(P)Rh(CR^1R^2C(O)R^3)$ (eq 25).

$$[(P)Rh]_2 + CHR^1R^2C(O)R^3 \rightarrow (P)Rh(CR^1R^2C(O)R^3) + (P)RhH \qquad (25)$$

$(P)Rh(CH_2OH)$ can undergo a slow self-condensation, giving rise to an equilibrium with the bridged ether complex (eq 26).

$$2(P)Rh(CH_2OH) \rightleftharpoons [(P)Rh(CH_2)]_2O \qquad (26)$$

The reaction of pivalaldehyde ($C(CH_3)_3C(O)H$) and benzaldehyde leads to $(P)Rh(C(O)C(CH_3)_3)$ and $(P)Rh(CH(OH)C_6H_5)$ as major products. Benzyl alcohols, such as $C_6H_5CH(OH)R$, where R = H, CH_3, or $C(O)C_6H_5$, also react with $[(P)Rh]_2$ to produce unstable α-hydroxyalkyl derivatives of the form $(P)Rh(CR(OH)C_6H_5)$. These derivatives dissociate into (P)RhH and $C_6H_5C(O)R$ species. Two mechanisms have been proposed for this reaction. The reactions of α-CH bonds are thought to occur by addition of the dimer to the enol form, while the reaction of aldehydic CH bonds is thought to proceed by the radical species $(P)Rh^\bullet$. No significant difference in this reaction has been observed by varying the porphyrin ligand.[151]

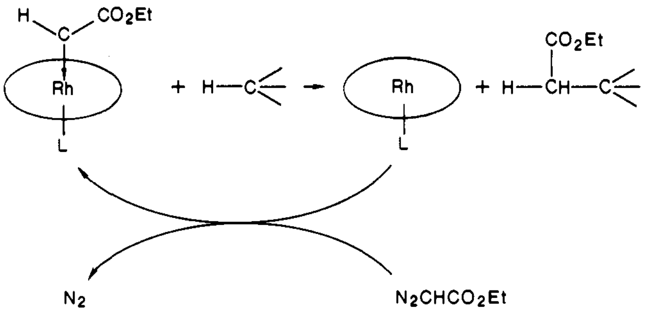
(P)Rh(R) complexes have also been synthesized by electrochemical methods. (TPP)Rh can be generated by the one-electron reduction of $[(TPP)Rh(L)_2]^+Cl^-$, where L is dimethylamine. The unstable (TPP)Rh monomer will rapidly dimerize in solvents such as THF or PhCN.[153] However, the formation of (TPP)Rh(R) is observed[154-156] if (TPP)Rh is generated in the presence of RX, HC≡CR, or $H_2C{=}CHR$. Twenty-one different (TPP)Rh(R) complexes have been synthesized by these methods.[154-157]

Electrochemical studies have provided a new route to the synthesis of (P)Rh(R) and have also provided insights into mechanisms for the reaction of (P)Rh and RX. The effect of both the R group and the X group of RX on the overall reaction rate constant for generation of (TPP)Rh(R) from (TPP)Rh and RX was measured by electrochemical methods.[155] The dependence of the reaction rate constant on X follows the trend $I > Br > F \geq Cl$, while the dependence on R follows the trend $CH_3 > C_2H_5 \approx n\text{-}C_3H_7 \approx n\text{-}C_4H_9 \approx n\text{-}C_5H_{11}$. On the basis of this and other data, an overall reaction scheme was proposed in which the (TPP)Rh radical attacked the carbon on the position α to the halide with subsequent loss of either $X^\bullet$ or X^-. This proposed mechanism differs in part, from reactions involving $[(P)Rh]_2$ and RX where a formation of (P)Rh(R) and (P)Rh(X) is observed.[142]

The radical nature of (P)Rh(R) formation from (P)Rh is evident in the reaction of (P)Rh with alkenes and alkynes. Reaction with HC≡CR or $H_2C{=}CHR$, where R = n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or n-C_6H_{13}, results in (TPP)Rh(R) formation with loss of the C_2 fragment.[156] This unexpected product reflects the high stability of the (P)Rh(R) complex.

Some aspects of $[(P)Ir]_2$ reactivity formed by photolysis of $(P)Ir(CH_3)$ were recently described.[146,152] The insertion of carbon monoxide between the iridium–hydride bond of (P)IrH does not occur, but $[(P)Ir]_2$ and $[(P)Rh]_2$ undergo similar reactions. In particular, $[(P)Ir]_2$ undergoes alkene insertion and oxidative addition of H_2 and alkyl C–H bonds.

SCHEME 23



Various aspects of the chemical reactivity of Co– and Rh–carbon derivatives have also been described.[136,150,158-169] The thermal reaction of aromatic alkyl Rh complexes leads to equal amounts of alkane and alkene according to eq 27.[150] Thermal reaction of

$$(P)Rh(CH(C_6H_5)C_2H_5) \rightarrow [(P)Rh]_2 + CH_3CH_2CH_2C_6H_5 + CH_3CH{=}CHC_6H_5 \qquad (27)$$

the same compounds under aerobic conditions yields an aldehyde or ketone (eq 28). (P)Rh(CHO) is found

$$(P)Rh(CH_2C_6H_5) \xrightarrow{\Delta,\ O_2} C_6H_5C(O)H + \tfrac{1}{2}[(P)Rh]_2 \qquad (28)$$

to react with (P)RhH, inducing reductive elimination of CH_3OH and subsequent insertion of CO to give the hydroxyacyl complex $(P)Rh(C(O)CH_2OH)$.[149] A highly regioselective electrophillic aromatic metalation can occur in the presence of rhodium(III) porphyrins with subsequent cleavage of the carbon–rhodium bond.[164,165] Reaction of (P)RhCl with benzene, anisole, toluene, and chlorobenzene in the presence of $AgClO_4$ or $AgBF_4$ gives $(P)Rh(p\text{-}XC_6H_4)$.[166] This reaction invariably occurs at the para position, while metalation of methyl benzoate leads to meta- and para-metalated isomers. The slow step in the reaction is most likely the coordination of the arene to give $[(P)Rh(arene)]^+$, which can subsequently undergo rapid loss of a proton (eq 29).

$$[(P)Rh]^+ + C_6H_5X \xrightarrow{\text{slow}} [(P)Rh(C_6H_5X)]^+ \xrightarrow{\text{fast}} [(P)Rh(p\text{-}XC_6H_4)] \qquad (29)$$

Activated arenes undergo photochemical homolysis of the metal–carbon bond and a halogen-induced heterolysis occurs to give p-haloarenes with regioselectivities higher than 99%.[166] A facile α-metalation of ketones occurs under mild conditions in the presence of (P)RhCl (eq 30).

$$(P)RhCl \xrightarrow{AgClO_4} (P)RhClO_4 \xrightarrow{RCH_2C(O)CH_3} (P)Rh(CH(R)COCH_3) \qquad (30)$$

Rhodium(III) porphyrins have also been used as catalysts for the decomposition of ethyl diazoacetate and the transfer of (ethoxycarbonyl)carbene to form cyclopropanes.[167,168] Large syn selectivities are obtained. Insertion of $CHCO_2Et$ into a C–H bond also occurs and is induced by decomposition of diazo esters catalyzed by sterically crowded rhodium(III) porphyrins.[169] The crucial step of this procedure is the transfer of a carbene fragment bound to the metalloporphyrin and its insertion into a C–H bond of the substrate. This reaction is shown in Scheme 23.

A large increase of homologation of the methyl group of alkanes and chloroalkanes is observed, while a good regioselectivity favors the transformation of p-xylene

TABLE 2. Half-Wave Potentials (V vs SCE) for the Reversible Reduction and Oxidation of (TPP)Co(R), (TPP)Rh(R), and (OEP)Ir(R)

	(TPP)Co(R)[a]			(TPP)Rh(R)				(OEP)Ir(R)	
R group	oxidation		reduction	oxidation[f]		reduction[g]		oxidation	reduction
p-$OCH_3C_6H_4$	1.30	1.04	-1.35						
p-$CH_3C_6H_4$	1.30	1.07	-1.37						
C_6H_5	1.41	1.09	-1.30	1.38	0.99	-1.40	-1.81		
p-BrC_6H_4	1.37	1.09	-1.36	1.38	0.99	-1.40	-1.81		
p-ClC_6H_4	1.32	1.07	-1.34	1.38	0.99	-1.40	-1.81		
p-$NO_2C_6H_4$	1.33	1.15	(-1.10)[e]	1.38	0.99	-1.40	-1.81		
$C_2H_5O_2C$	1.27[b]	1.04[b]							
CH_3			-1.330[c]	1.34	0.96	-1.43	-1.85	0.68[d]	
C_2H_5	1.19[b,d]	0.98[b,d]	-1.300[c]			-1.42			
n-C_3H_7		0.795[c]	-1.310[c]			-1.42	-1.23	0.65	-1.88
n-C_4H_9		0.780[c]	-1.320[c]			-1.42			
i-C_4H_9		0.785[c]	-1.305[c]						
C_6H_{11}		0.725[c]	-1.320[c]						
$CH{=}CH(C_6H_4)$		0.775[c]	-1.318[c]						
$COCH_3$				1.33[f,h]	1.03[f]	-1.37	-1.78		
CH_2Cl				1.38	0.92	-1.42			
$CHCl_2$						-1.41			
CCl_3						-1.41			
C_8H_{13}								0.68[i]	-1.79[i]

[a] Values measured in CH_2Cl_2, 0.1 M TBAP (ref 55 and 56) or in Me_2SO, 0.1 M TBAP (ref 120) where indicated. [b] Measured at a Pt electrode vs Ag/AgCl reference electrode (ref 55). [c] Measured in Me_2SO at a Pt electrode (ref 120). [d] At -40 °C. [e] Reduction involves nitro group. [f] Measured in PhCN, 0.1 M TBAP (ref 196). [g] Measured in THF, 0.2 M TBAP (ref 154-157 and 196). [h] Irreversible reaction. Value presented is E_{pa} at a scan rate of 0.1 V/s. [i] Reference 128. Value given in THF.

and mesitylene into dihydrocinnamates.

The irradiation of $(OEP)Co(CH_2C_6H_5)(PR_3)$, where $PR_3 = PPh_3$, $P(C_2H_5)Ph_2$, PMe_2Ph, $P(n\text{-}C_4H_9)_3$, or $P(c\text{-}C_6H_{11})_3$, was carried out in the presence of the free radical trap TEMPO, and the Co–C bond dissociation energy was determined as a function of the axially bound ligand[170] (eq 31).

$$(OEP)Co^{III}(CH_2C_6H_5)(PR_3) + TEMPO \xrightarrow{h\nu} PhCH_2\text{-}TEMPO + (OEP)Co^{II}(PR_3) \quad (31)$$

B. Photochemical Reactivity of (P)Co(R)

Photolysis of (TPP)Co(R) in the presence of molecular oxygen yields new complexes that have been characterized by ^1H NMR and UV–visible spectroscopy as (TPP)Co(OOR), where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_4H_9, $CH_2C_6H_5$, or $(CH_2)_2C_6H_5$ (eq 32).[120]

$$(TPP)Co(R) + O_2 \xrightarrow[\text{visible}]{h\nu} (TPP)Co(OOR) \quad (32)$$

More recently, Kendrick and Al-Akhadar[161] measured the rate of dioxygen insertion into the Co–C bond of (P)Co(R)(L) and reported that the observed rate constants for this reaction correlated with the cobalt–carbon bond dissociation energies of the complexes (eq 33). This was true for (P)Co(R)(L) complexes, where P = OEP, R = $CH_2C_6H_5$, C_2H_5, or CH_3, and L = py, PPh_3, $PEtPh_2$, or $P(n\text{-}C_4H_9)_3$.

$$(P)Co(R)(L) + O_2 \rightarrow (P)Co(OOR)(L) \quad (33)$$

Each $(P)Co^{III}(OOR)(L)$ complex was isolated and characterized by UV–visible and ^1H NMR spectroscopic techniques. Irradiation of $(P)Co(CH_2CH_2OH)$ or $(P)Co(CH_2CH_2CH_2OH)$, where P = etioporphyrin I, produces acetaldehyde or acetone[118] (eq 34 and 35).

$$(P)Co(CH_2CH_2OH) \xrightarrow{h\nu} (P)Co^{II} + CH_3CHO \quad (34)$$

$$(P)Co(CH_2CH_2CH_2OH) \xrightarrow{h\nu} (P)Co^{II} + CH_3COCH_3 \quad (35)$$

C. Electrochemistry of σ-Bonded Cobalt and Rhodium Porphyrins

Numerous reports of σ-bonded cobalt, rhodium, and iridium porphyrins have appeared in the literature, but the electrochemistry of these complexes is limited to only a few studies. Three laboratories have reported the electrochemistry of (TPP)Co(R),[55,56,120,171,172] two laboratories have reported the electrochemistry of (OEP)Ir(R),[116,128,173] and only a single laboratory has reported the electrochemistry of (TPP)Rh(R).[154-157] A summary of reversible half-wave potentials from these studies is given in Table 2. Virtually all of the reactions are reversible on the cyclic voltammetric time scale although in some cases either low temperature or rapid scan rates are needed to achieve this.

The electroreduction of organocobalt complexes generally leads to a cleavage of the cobalt–carbon bond,[174-176] and this also seems to be the case for electroreduction of alkyl–cobalt complexes of (TPP)Co(R).[120] In contrast, a rapid cobalt–carbon bond cleavage does not occur after electroreduction of (TPP)Co(R), where R is a σ-bonded aryl group,[56] and reversible half-wave potentials have been reported.

The potentials for reduction of (TPP)Co(R) are similar to those for reduction of (TPP)Rh(R) and vary little with the type of σ-bonded alkyl ligand. On this basis it can be suggested that the initial reduction of both complexes involves an orbital of the conjugated π system. However, the ultimate product of (TPP)Co(R) reduction when R is an alkyl group is $[(TPP)Co^I]^-$.[120] A similar formation of $[(OEP)Ir^I]^-$ is observed after controlled-potential reduction of $(OEP)Ir(C_8H_{13})$[128] but there is no evidence for $[(P)Rh^I]^-$ generation by electrochemical methods. This is due in large part to the rapid chemical reactions involving electrochemically generated (TPP)Rh.[153-157,177]

A cleavage of the metal–carbon bond does not occur for $[(P)Al(R)]^-$, $[(P)In(R)]^-$, $[(P)Ga(R)]^-$, $[(P)Ge(R)_2]^-$, or $[(P)Rh(R)]^-$ nor does it occur upon formation of $[(P)Al(R)]^{2-}$, $[(P)In(R)]^{2-}$, $[(P)Ga(R)]^{2-}$, or [(P)Rh-

(R)]$^{2-}$.[178-181] A stable [(P)Fe(C_6H_5)]$^-$ complex is also generated on reduction of (P)Fe(C_6H_5),[29] but rapid cleavage of the iron–carbon bond occurs after the first reduction of (P)Fe(R) complexes, where R = C_6F_5 or C_6F_4H.[15] These differences in stability may result from differences in the site of electron transfer. The reduction of cobalamin[175] and (P)Fe(C_6F_5)[15] involves the orbitals of the metal ion. This is not the case for the group 13 σ-bonded complexes, where anion radicals and dianions are formed.[178-181] An anion radical may also be formed as a transient species in the initial reduction of (TPP)Co(R), and, if so, this would contribute to an increased stability of [(TPP)Co(R)]$^-$.

Seven compounds of (TPP)Co(R) have been investigated at a rotating-disk electrode in Me_2SO containing 0.1 M TBAP as supporting electrolyte.[120] Each compound underwent an initial one-electron reduction and gave a current–voltage curve whose wave analysis indicated a reversible to quasi-reversible electron transfer as shown in eq 36. This reduction was followed by a

$$\text{(TPP)Co(R)} + e^- \rightleftarrows [\text{(TPP)Co(R)}]^- \qquad (36)$$

cleavage of the cobalt–carbon bond (reaction 37) and

$$[\text{(TPP)Co(R)}]^- \rightarrow \text{(TPP)Co} + R^- \qquad (37)$$

the addition of a second electron to generate [(TPP)-Co^I]$^-$ (reaction 38) This latter reaction occurs at −0.80

$$\text{(TPP)Co}^{II} + e^- \rightleftarrows [\text{(TPP)Co}^{I}]^- \qquad (38)$$

V in Me_2SO[182,183] so that the overall reaction thus corresponded to the two-electron reduction of (TPP)Co(R) as shown in eq 39.[120]

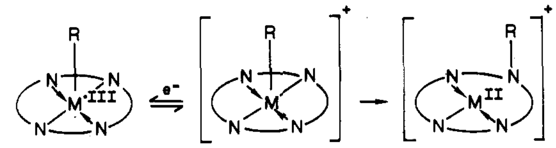
$$\text{(TPP)Co(R)} + 2e^- \rightleftarrows [\text{(TPP)Co}^{I}]^- + R^- \qquad (39)$$

Potentials for reduction of (TPP)Co(R) vary little with changes in the R group or the solvent system. This is illustrated by the data in Table 2, which lists $E_{1/2}$ for the reduction of σ-bonded alkyl complexes in Me_2SO and σ-bonded aryl complexes in CH_2Cl_2. Values of $E_{1/2}$ vary between −1.30 and −1.37 V vs SCE in Me_2SO, and a similar range of potentials (between −1.30 and −1.36 V) is noted in CH_2Cl_2. These latter values were obtained by cyclic voltammetry at a Pt electrode in CH_2Cl_2. This study was limited to aryl-bonded complexes of (TPP)Co(R), where R = p-XC_6H_4 and X = OCH_3, CH_3, Br, or Cl.[56] The reduction of (TPP)Co(p-$NO_2C_6H_4$) was also investigated in CH_2Cl_2[56] but this compound underwent a reaction at the NO_2 group of the σ-bonded ligand. A cleavage of the Co–R bond was not reported for any of the complexes but may have occurred on time scales slower than those utilized in cyclic voltammetry.

The oxidation of (TPP)Co(R) was first investigated by rotating-disk voltammetry in Me_2SO.[120] Potentials in this coordinating solvent are shifted in a negative direction by 200–300 mV from values in CH_2Cl_2. A similar shift of potential is observed upon adding Me_2SO to CH_2Cl_2 solutions containing (TPP)Co(R)[184] and this suggests the coordination of Me_2SO to oxidized [(TPP)Co(R)]$^+$. The reduction of (TPP)Co(R) is not shifted on going from CH_2Cl_2 to Me_2SO (see Table 2) and this suggests only a small interaction of Me_2SO with the neutral form of the complex.

The first mechanistic study on the electrooxidation of σ-bonded cobalt porphyrins was reported by Dolphin[55] for (TPP)Co(R) complexes, where R was C_2H_5 and $C_2H_5O_2C$. At low temperatures, the reversible formation of [(TPP)Co(R)]$^+$ and [(TPP)Co(R)]$^{2+}$ was noted. However, at room temperature singly oxidized [(TPP)Co(R)]$^+$ was not stable, and a metal-to-porphyrin nitrogen migration of the R group occurred.

SCHEME 24



Metal-to-nitrogen migrations occur after chemical or electrochemical oxidation of σ-bonded iron and cobalt porphyrins. The reactions involving iron are discussed in previous sections. The initial sequence of steps for the electrochemically initiated conversion of (TPP)-Co^{III}(R) to [(N-RTPP)Co^{II}]$^+$ is similar to that reported[29] for electrochemically initiated conversion of (P)Fe(R) to [(N-RP)Fe]$^{2+}$ and the migration step is schematically illustrated in Scheme 24 for M = Co and Fe.

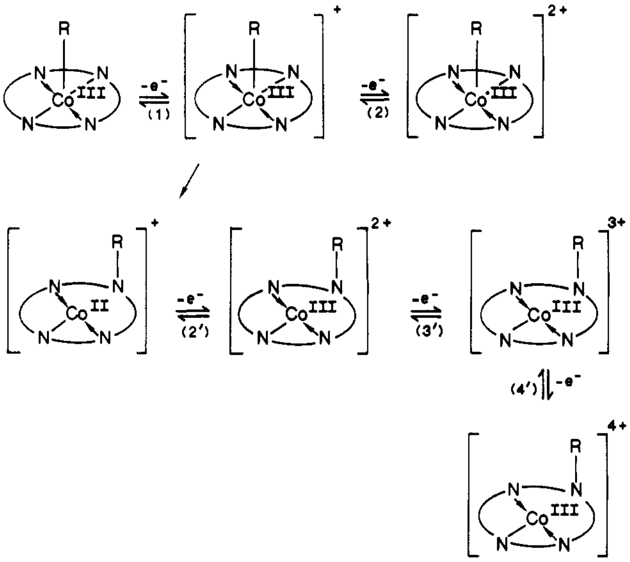
The migration of R from (TPP)Co(R) to (N-RTPP)Co^{II}Cl can proceed by either a one- or a two-electron intermediate.[55] This was investigated by Callot,[103] who synthesized a series of different (TPP)-Co(R) metalloporphyrins and demonstrated that the reaction proceeded via the one-electron-transfer pathway.[103,104] The investigated cobalt metalloporphyrins contained σ-bonded aryl groups of the type p-XC_6H_4, where X = OCH_3, CH_3, H, Br, Cl, and NO_2.

Potentials for oxidation of the above complexes were reported by Callot and Gross,[56] and the kinetics of aryl group migration and/or demetalation after chemical oxidation were related to the nature of the R group on the phenyl ligand. However, a mechanistic detail of the actual electrooxidation was not provided nor was the nature of any intermediates in the electrochemical reaction investigated. In addition, the conclusions of Callot and Gross are not internally self-consistent with their own data for oxidation of the (N-RTPP)Co^{II}Cl complexes[56] or with other related data in the literature.[55,185] This is due to the fact that the products of (TPP)Co(R) oxidation were not monitored during the actual electron-transfer step but rather were characterized after a chemical reaction involving (TPP)Co(R) and [(p-$BrC_6H_4)_3N]^+SbCl_6^-$ or CCl_3COOH/O_2.

The steps associated with the electrooxidation of (TPP)Co(R) and electrochemically or chemically synthesized (N-RTPP)Co^{II}Cl are summarized in Scheme 25.

Between two and four oxidations of (TPP)Co(R) may occur, depending upon the temperature, the specific R group, and the nature of the solvent system. At fast scan rates or low temperature, a migration will not occur before the abstraction of a second electron and the oxidation sequence is via reactions 1 and 2 in Scheme 25. This was first illustrated by Dolphin[55] for the oxidation of (TPP)Co(C_2H_5) in CH_2Cl_2. At −40 °C, this complex is reversibly oxidized at $E_{1/2}$ = 0.98 and 1.19 V. A slow migration step is also observed for σ-bonded aryl porphyrins of the type (TPP)Co(p-XC_6H_4),[56] but reversible room-temperature half-wave potentials have been reported in the range 1.04–1.15 V for the first oxidation (reaction 1, Scheme 25) and 1.30–1.41 V for

SCHEME 25



the second oxidation (reaction 2).

The only electrochemically generated N-substituted cobalt porphyrin for which oxidation potentials are reported is $[(N\text{-}C_2H_5TPP)Co^{II}]^+$.[55] This complex was generated from $(TPP)Co(C_2H_5)$ (at $E_p = 0.98$ V) and is reversibly oxidized in two steps, which occur at $E_{1/2} = 1.10$ and 1.70 V vs SCE in CH_2Cl_2. In contrast, chemically synthesized $(N\text{-}CH_3TPP)Co^{II}Cl$ has three oxidations (reactions 2′, 3′, and 4′, Scheme 25), which occur in acetonitrile at $E_{1/2} = 0.77$, 1.30, and 1.60 V vs SCE.[185] Finally, only a single oxidation peak (which occurs in the range 1.10–1.21 V in CH_2Cl_2) has been reported for chemically synthesized (*N*-RTPP)CoCl, where R = $p\text{-}XC_6H_4$.

Although many similarities exist between the Fe and Co σ-bonded metalloporphyrins, there are sufficient differences between the two series. For example, the cobalt-to-nitrogen migration of (TPP)Co(R) involves the prior formation of a Co(III) cation radical.[55] In contrast, the iron-to-nitrogen migration of (P)Fe(R) involves the generation of an Fe(IV) intermediate.[29,30] The first oxidation of (TPP)Co(R) appears to be virtually independent of the R group donicity,[55] but this may be due to the relatively small differences between the investigated alkyl and aryl σ-bonded complexes.

The mechanisms for oxidation of (TPP)Co(R) and (TPP)Fe(R) also differ with respect to the fate of the electrogenerated N-substituted porphyrin. The electrogenerated *N*-alkyl or *N*-aryl iron porphyrins that have been investigated to date[29] are easier to oxidize than the neutral σ-bonded complexes. This results in an overall two-electron oxidation of (P)Fe(R) with the ultimate formation of an Fe(III) *N*-alkyl or *N*-aryl complex. In contrast, the generated *N*-alkyl Co(II) complex may or may not be more difficult to oxidize than the neutral σ-bonded cobalt(III) porphyrin and a second electron may or may not be spontaneously abstracted from Co(II) after the migration step. This will depend upon the specific R group.

The reversible oxidations of $(TPP)Co(C_2H_5)$[55] at −40 °C in CH_2Cl_2 occur at 0.98 and 1.19 V vs SCE and lead to the generation of $[(TPP)Co(C_2H_5)]^+$ and $[(TPP)Co(C_2H_5)]^{2+}$ in solution. On the other hand, $[(N\text{-}C_2H_5TPP)Co^{II}]^+$ is oxidized at $E_{1/2} = 1.10$ and 1.70 V. Thus, at low potential scan rates or at room temperature, three one-electron oxidations of $(TPP)Co(C_2H_5)$ are observed.

The potential difference between oxidation of $(TPP)Co^{III}(C_2H_5)$ ($E_p = 0.98$ V) and oxidation of $[(N\text{-}C_2H_5TPP)Co^{II}]^+$ ($E_{1/2} = 1.10$ V) is small, and this suggests that by the appropriate selection of the σ-bonded ligand one should be able to vary the overall number of electrons transferred in the electrochemically initiated migration step. The data of Callot and Gross[56] seem to add further weight to this suggestion. For example, the reversible oxidation of $(TPP)Co(C_6H_5)$ occurs at $E_{1/2} = 1.09$ V in CH_2Cl_2 and is virtually identical with the $E_{1/2}$ of 1.10 V for oxidation of $(N\text{-}C_6H_5TPP)Co^{II}Cl$ in the same solvent–supporting electrolyte system.[56]

Crucial to the question of a global one- vs a two-electron oxidation of (P)Co(R) is the nature of the anion associated with $[(N\text{-}RTPP)Co^{II}]^+$. Potentials for oxidation of $[(N\text{-}C_6H_5TPP)Fe^{II}]X$ vary from −0.06 V when X = ClO_4^- to 0.44 V when X = Cl^-.[29] A similar shift in $E_{1/2}$ should occur for electrogenerated *N*-alkyl or *N*-aryl cobalt(II) complexes, and values of $E_{1/2}$ for this reaction should depend upon the anion of the supporting electrolyte. On the other hand, the oxidation potential of (TPP)Co(R) should also depend upon the anion of the supporting electrolyte, and this variable might also influence the electrooxidation mechanism.

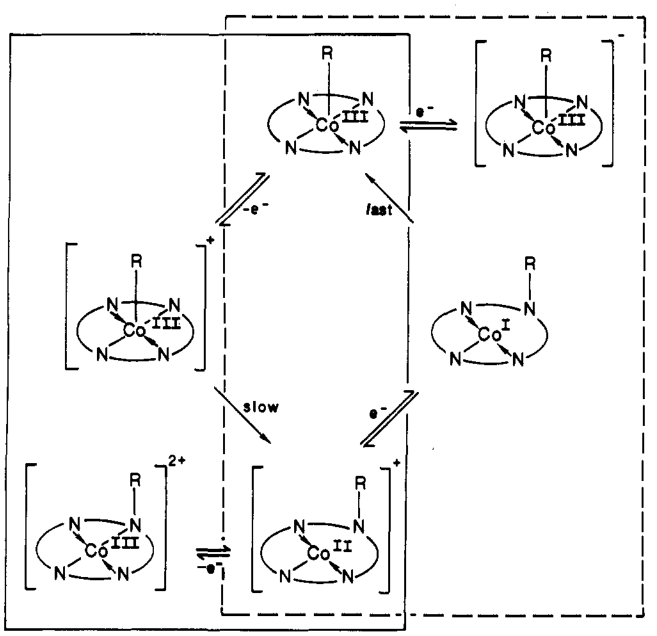
Half-wave potentials for (P)Fe(R) oxidation also vary significantly with the basicity of the porphyrin ring. For example, $((CN)_4TPP)Fe(C_6H_5)$ is oxidized at 1.03 V[15] while the initial electrooxidation of $(OEP)Fe(C_6H_5)$ occurs at 0.48 V.[29] A similar variation should occur for cobalt complexes and this difference in $E_{1/2}$ may affect both the migration step and the oxidation mechanism. However, no information is presently available about the effects of porphyrin structure or porphyrin ring basicity on the cobalt-to-nitrogen migration of (P)Co(R). Finally, the electrochemistry of σ-bonded cobalt metalloporphyrins is closely related to that of the *N*-alkyl cobalt porphyrins. This is discussed in the following section of the review.

D. Electrochemistry of σ-Bonded Iridium Porphyrins

Only a few σ-bonded Ir(III) porphyrins have been electrochemically investigated. The most detailed studies were carried out on complexes of $(OEP)Ir(n\text{-}C_3H_7)$,[173] $(OEP)Ir(n\text{-}C_3H_7)(L)$,[173] and $(OEP)Ir(C_8H_{13})$,[128] the latter of which was also structurally characterized. An earlier electrochemical study of $(OEP)Ir(CH_3)(L)$, where L = CO, CN^-, py, NH_3, or *N*-MeIm, was published[116] but was incorrect in assigning the site of the electron-transfer processes. Specifically, the oxidations at the porphyrin π ring system to generate $[(OEP)Ir(n\text{-}C_3H_7)(L)]^+$ were incorrectly assigned as reductions to generate $[(OEP)Ir]^-$.

Later more detailed studies demonstrated that $(OEP)Ir(n\text{-}C_3H_7)$[173] and $(OEP)Ir(C_8H_{13})$[128] undergo reversible oxidations and reductions, the latter of which occurs at $E_{1/2} = 0.68$ and −1.79 V vs SCE in THF, 0.1 M TBAP. The process at 0.68 V was clearly demonstrated to be an oxidation by rotating-disk voltammetry while the process at −1.79 V was shown to be a reduction.[128] The electrooxidation was reversible on the cyclic voltammetric and the bulk electrolysis time scales (1–5

SCHEME 26



min) and involved an abstraction of one electron from the axially bound ligand.

The same σ-bonded complex could also be reduced via a reversible one-electron-transfer process.[128] $[(OEP)Ir(C_8H_{13})]^-$ was generated as a transient product of the electroreduction but this porphyrin π anion radical was not sufficiently stable to be isolated and $[(OEP)Ir]^-$ was ultimately formed as a product of the reaction after a global two-electron reduction.

$(OEP)Ir(C_8H_{13})$ is able to bind CO to form the six-coordinate $(OEP)Ir(C_8H_{13})(CO)$ species.[128] This compound also undergoes reversible oxidations and reductions, which occur at $E_{1/2}$ = 0.80 and −1.65 V vs SCE in THF, 0.1 M TBAP. The oxidation at 0.80 V is reversible on the cyclic voltammetric time scale but the final product of oxidation was characterized as $(OEP)Ir(CO)(ClO_4)$. In contrast, the reductions lead to more stable products, and the anion radical, $[(OEP)Ir(C_8H_{13})(CO)]^-$, was spectrally characterized after bulk electrolysis of $(OEP)Ir(C_8H_{13})(CO)$.

E. Cobalt–*N*-Alkyl and Cobalt–*N*-Aryl Porphyrins

The physical and structural properties of N-substituted cobalt porphyrins have been extensively investigated,[185-192] but the electrochemistry of these complexes has received only little attention in the literature.[56,70,185,192] However, recently discovered biological implications of *N*-alkyl porphyrins[26,64,65,67-70] have generated a renewed interest and significance in understanding the chemical and electrochemical behavior and the physicochemical properties of these complexes.

The migrations of electrogenerated $[(TPP)Fe(C_6H_5)]^+$ and $[(OEP)Fe(C_6H_5)]^+$ have been discussed in section III of this review. A similar reversible migration sequence also occurs for (P)Co(R)[56] and is illustrated in Scheme 26.

Preliminary reports of electrochemically initiated alkyl and aryl migration are quite exciting and along with further studies should provide the data for interesting and significant insights into the chemical and electrochemical behavior of N-substituted porphyrins. A recent publication indicates that the electron-transfer reactions of *N*-alkyl and *N*-aryl porphyrins is not followed by a cleavage of the N-substituted group and that reversible oxidations and reductions are obtained.[72] The M(II)/M(III) couple and formal M(II)/M(I) couple of *N*-methyl porphyrin derivatives have been obtained for complexes with Co,[185] Fe,[69,72] and Mn[72,185] central metals but none of these reactions have been spectrally monitored. Thus, the exact site of electron transfer in cobalt porphyrins is still open to question, especially for complexes reduced below the formal M(II) state or oxidized above the formal M(III) state.

F. Electrochemistry of σ-Bonded Rhodium(III) Porphyrins and Related N-Substituted Rhodium(II) Complexes

Numerous publications have appeared in the literature that report the synthesis of Rh(III) and Rh(II) porphyrins. The Rh(II) porphyrins are dimeric[153] while the Rh(III) porphyrins are monomeric. These latter complexes have been characterized as containing a σ-bonded carbon group in the axial position or as ionic complexes of the type (P)RhCl, (P)Rh(L)Cl, or $[(P)Rh(L)_2]^+Cl^-$.[153,193-196]

(TPP)Rh(R) is reduced by one or two one-electron-transfer steps in nonaqueous media. The first reduction of $(TPP)Rh(CH_3)$ occurs between −1.39 and −1.44 V vs SCE, depending on solvent, while the second reduction occurs at −1.85 V (in THF) or −1.87 V vs SCE (in PhCN) (see Table 2). Two reductions also occur for $(TPP)Rh(COCH_3)$, but $(TPP)Rh(CH_2Cl)$ and $(OEP)Rh(CH_3)$ undergo only a single electroreduction within the potential range of the solvent.

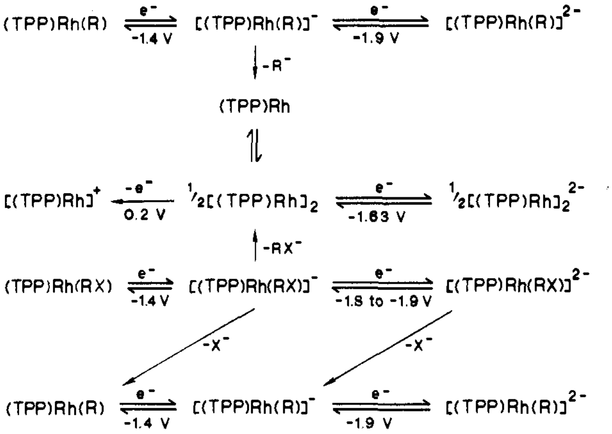
The reduction of $[(TPP)Rh(L)_2]^+Cl^-$, where L = dimethylamine, generates a highly reactive Rh(II) species,[154] which dimerizes to generate $[(TPP)Rh]_2$ in PhCN, THF, or pyridine. However, the Rh(II) radical does not dimerize in CH_2Cl_2 but instead reacts with the solvent to form $(TPP)Rh(CH_2Cl)$.[154] This was the first example of a σ-bonded carbon–rhodium(III) species whose synthesis is electrochemically initiated. $(TPP)Rh(CH_2Cl)$ was isolated after bulk electrolysis of $[(TPP)Rh(L)_2]^+Cl^-$ in CH_2Cl_2 and characterized by cyclic voltammetry and infrared, ^1H NMR, and UV-visible spectroscopy.[154] The properties of $(TPP)Rh(CH_2Cl)$ are virtually identical with those of $(TPP)Rh(CH_3)$.

Potentials for the reversible reduction of 16 different (TPP)Rh(R) complexes where R is an alkyl group vary little with the nature of R.[155] This is shown in Table 2, where values of $E_{1/2}$ for representative complexes range only between −1.37 and −1.43 V vs SCE. There is no change upon going from R = CH_3 to R = n-C_5H_{11} nor is there a change in $E_{1/2}$ upon going from R = CH_3 to R = CH_2Cl, $CHCl_2$, or CCl_3.

A second reduction of (TPP)Rh(R) is observed in THF or PhCN, and for $(TPP)Rh(CH_3)$ this reaction occurs at −1.85 V vs SCE. This results in a separation of 420 mV between the first and second reduction, which is consistent with the formation of a π anion radical and a dianion. A similar 410-mV separation is noted for $(TPP)Rh(COCH_3)$ in THF (see Table 2).

The oxidations of $(TPP)Rh(CH_3)$ occur at 0.96 and 1.34 V while those of $(TPP)Rh(CH_2Cl)$ occur at 0.92

SCHEME 27



and 1.38 V. Both sets of data are consistent with the formation of cation radicals and dications, and this is also indicated by the UV–visible and ESR data of the oxidation products.

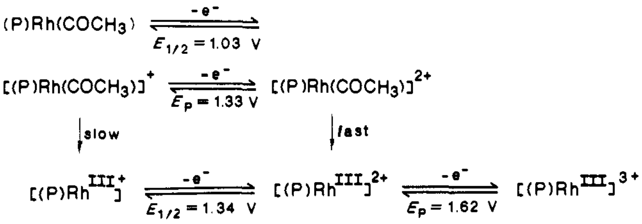
The electrochemistry and reactivity of 17 different (TPP)Rh(R) and (TPP)Rh(RX) complexes were also reported,[157] where R = C_6H_5 or C_nH_{2n+1} (n = 1–6) and RX = $C_nH_{2n}Cl$ (n = 3–5), $C_nH_{2n}Br$ (n = 3–5), or $C_nH_{2n}I$ (n = 3–6). The nature of the σ-bonded R or RX group was shown to determine the overall reductive properties of (TPP)Rh(R) or (TPP)Rh(RX). The bound alkyl halide of some (TPP)Rh(RX) complexes could be electroreduced without a cleavage of the rhodium–carbon bond, and this resulted in the electrochemically initiated conversion of (TPP)Rh(RX) to (TPP)Rh(R).[157] This behavior is presented in Scheme 27, which summarizes the electrochemistry of these compounds in THF.

Scheme 27 indicates that reduction of a σ-bonded Rh(III) porphyrin can occur at the porphyrin macrocycle to generate porphyrin π anion radicals and dianions or, alternatively for the case of (TPP)Rh(RX), the reduction may occur at the σ-bonded axial ligand to generate (TPP)Rh(R). Values of $E_{1/2}$ for reduction of the bound RX ligand are significantly less negative than potentials for reduction of free RX or RX_2 under the same solution conditions.

Three oxidation peaks are observed for (TPP)Rh($COCH_3$) in PhCN.[196] The first occurs at 1.03 V. This reaction is reversible and seems to involve an electron abstraction involving the acetyl group rather than the porphyrin π ring system. The second occurs at E_{pa} = 1.33 V and is followed by a rapid chemical reaction. This oxidation involves the abstraction of one electron and is followed by a third reversible oxidation at ~1.52 V. It was originally thought that a migration of the $COCH_3$ group occurred but more detailed studies of the reaction by thin-layer spectroelectrochemistry indicated that both the singly oxidized and doubly oxidized species could undergo a rhodium–carbon bond cleavage to generate $[(TPP)Rh^{III}]^+$ or $[(TPP)Rh^{III}]^{2+}$. The mechanism for this reaction is given in Scheme 28.[196]

Potentials for the first reduction and first oxidation of (TPP)Rh(R) are virtually identical with reversible half-wave potentials for the reduction and oxidation of (TPP)Co(R) in CH_2Cl_2. For five different Co(III) complexes (where R is a substituted aryl group) values of $E_{1/2}$ range between −1.30 and −1.37 V for reduction and between 1.04 and 1.15 V for oxidation. The initial oxidation of (TPP)Co(R) is postulated to occur at the porphyrin π ring system,[55] and similar conclusions result from the spectral data on $[(TPP)Rh(R)]^{+}$.[157,196] No information is available regarding the site of reduction in $[(TPP)Co(R)]^-$, but for $[(TPP)Rh(R)]^-$, the initial electroreduction seems to involve reduction at the σ-bonded group rather than formation of Rh(II).

SCHEME 28



The addition of a nitrogenous base to (P)Rh(R) is also possible and the six-coordinate (P)Rh(CH_3)(L) complex has been spectrally characterized where L is a bound amine group[60] or triphenylphosphine.[197] The electrochemistry of the six-coordinate triphenylphosphine complexes and the effect of the sixth axial ligand on potentials for reduction of (P)Rh(R)(PPh_3) have also been investigated.[197]

The binding of triphenylphosphine by (P)Rh(R) leads to stable solutions of (P)Rh(R)(L). These six-coordinate compounds are reduced at potentials that are cathodically shifted from $E_{1/2}$ values for reduction of (P)Rh(R) in the same solvent–supporting electrolyte system.[197] The formation of $[(P)Rh(R)(L)]^-$ is postulated to occur after addition of one electron to (P)Rh(R)(L), but a subsequent cleavage of the rhodium–carbon bond occurs after formation of the porphyrin π anion radical. This reductive behavior of (TPP)Rh(R)(PPh_3) contrasts with that of (TPP)Rh(R), which undergoes two electroreductions and gives a stable π anion radical.

It is interesting to compare the chemical reactivity of singly (or doubly) oxidized (TPP)Rh($COCH_3$) with singly oxidized (P)Co(R) and (P)Fe(R), on the one hand, and singly oxidized (P)Al(R), (P)Ga(R), (P)In(R), and (P)Ge$(R)_2$, on the other hand. All of the oxidized compounds are unstable and each compound undergoes a rapid cleavage of the metal–carbon bond. They differ, however, in that the iron and the cobalt derivatives undergo a metal-to-nitrogen migration resulting in the corresponding N-substituted porphyrin with an M(II) center, but this migration does not occur for $[(P)Al(R)]^+$, $[(P)In(R)]^+$, $[(P)Ga(R)]^+$, or $[(P)Ge(R)_2]^+$. This lack of migration is presumably due to the absence of an M(II) oxidation state needed to form the main-group *N*-alkyl porphyrin. A Rh(II) oxidation state is readily accessible and thus one would expect to observe the electrochemically initiated synthesis of $[(N\text{-RP})Rh^{II}]^+$.

Especially relevant to studies of (P)Rh(R) are investigations of a possible reverse nitrogen-to-rhodium migration of any electrochemically generated N-substituted complex. The synthesis of (OEP)Rh(CH_3) has been reported to proceed via a chemically generated (N-CH_3OEP)Rh^I species.[60] A similar migration occurs for Co(I) and (formally) Fe(I) porphyrins and thus one might predict an electrochemically initiated migration for N-substituted porphyrin complexes of Rh. However, genuine N-substituted Rh(II) porphyrins have never been isolated.

VI. Aluminum, Gallium, Indium, and Thallium

A. Synthesis and Reactivity

A number of group 13 σ-bonded metalloporphyrins have now been synthesized. The reaction of Grignard reagents or alkyl- and aryllithium with (P)MX gives rise to the corresponding monoalkyl or monoaryl (P)M(R) derivatives according to eq 40, where X = halide, M′ = Mg, and Y = halide, or M′ = Li with no Y group.

$$(P)MX + RM'Y \rightarrow (P)M(R) + XM'Y \qquad (40)$$

This method has been used for the synthesis of σ-bonded metal–alkyl or metal–aryl porphyrins of gallium,[178,198] indium,[199–201] thallium,[202] and aluminum.[181] The σ-bonded derivatives synthesized by this procedure have generally been isolated in good yields, and no significant differences are observed between the four different types of metal complexes. However, the (P)Al(R) complexes are easily photodecomposed.[181]

Aluminum[109,110] and thallium[202] porphyrins containing a metal–carbon σ bond have also been synthesized by treating the porphyrins with organometallic compounds such as $Al(C_2H_5)_3$ or $Tl(CH_3)(OCH_3)_2$ (eq 41 and 42).

$$(P)H_2 \xrightarrow{Al(C_2H_5)_3} (P)Al(C_2H_5) \qquad (41)$$

$$(P)H_2 \xrightarrow{Tl(CH_3)(CH_3CO_2)_2} (P)Tl(CH_3) \qquad (42)$$

Substitution reactions of $(TPP)Al(C_2H_5)$ in benzene with hindered phenols are accelerated dramatically by irradiation with visible light to form metalloporphyrins with the corresponding phenoxy group bound to aluminum[158] (eq 43).

$$(TPP)Al(C_2H_5) + HOC_6H_4OCH_3 \xrightarrow{h\nu} (TPP)Al\text{-}OC_6H_4OCH_3 + C_2H_6 \qquad (43)$$

The reactivity of σ-bonded aluminum and indium porphyrins toward carbon dioxide has been reported. The photostimulated interaction of CO_2 with $(TPP)Al(C_2H_5)$ in the presence of *N*-methylimidazole leads to the formation of $(TPP)Al(CO_2C_2H_5)$ (eq 44), which

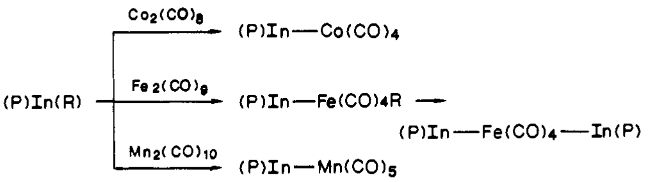
$$(TPP)Al(C_2H_5) \xrightarrow{CO_2} (TPP)Al(CO_2C_2H_5) \qquad (44)$$

was characterized in situ.[109] Similar photochemical insertions have been reported for $(P)In(CH_3)$, where P is OEP or TPP (eq 45).[201] The same $(P)In(CO_2CH_3)$

$$(P)In(CH_3) \xrightarrow{CO_2,\ py,\ h\nu} (P)In(CO_2CH_3) \qquad (45)$$

product has been obtained by reaction of acetic acid and a σ-bonded alkylindium(III) porphyrin or by the reaction of acetic acid and the aquohydroxoindium(III) porphyrin, $(P)In(OH)(H_2O)$. An X-ray structure of $(OEP)In(CO_2CH_3)$[201] demonstrates that the coordination polyhedron is intermediate between an end-on coordination like that found in $(TpTP)Fe(CO_2CH_3)$[203] and a bidentate coordination like that found in $(TPP)Nb(O)(CO_2CH_3)$[204] or $(OEP)Zr(CO_2CH_3)_2$.[205] Both irradiation and pyridine are required for insertion of CO_2 into the indium–carbon σ bond of $(P)In(CH_3)$ but the six-coordinate $(P)In(CH_3)(py)$ complex is not observed, even in neat pyridine.

SCHEME 29



It has been suggested that pyridine coordinates to the reduced indium porphyrin, leading to a stable six-coordinate $[(P)In(CH_3)(py)]^{\bullet -}$ species.[201] This contrasts with results obtained for $(TPP)Al(C_2H_5)$, where six-coordinate adducts are formed upon addition of imidazole.[109]

Insertion of sulfur dioxide into a metal–carbon bond has been described for σ-bonded indium[206,207] and gallium[208] porphyrins and leads to $(P)M(SO_2R)$ sulfinato derivatives. These complexes are easily oxidized by a stream of oxygen to give the corresponding sulfonato $(P)M(SO_3R)$ derivatives, where M is Ga or In and R is an alkyl or an aryl group (eq 46). Sulfinato and sulfonato indium(III) porphyrins can also be isolated by oxidation of the corresponding (P)In(SR) derivatives. In addition, acid hydrolysis of (P)GaCl using the appropriate sulfonic acid leads to the identical sulfonato gallium(III) compounds.[208]

$$(P)M(R) \xrightarrow{SO_2} (P)M(SO_2R) \xrightarrow{O_2} (P)M(SO_3R) \qquad (46)$$

The $(P)In(SO_2R)$ and $(P)In(SO_3R)$ complexes have very flexible structures. The $(P)Ga(SO_3R)$ or $(P)Ga(SO_2R)$ analogues have *O*-sulfonate or *O*-sulfinate coordination of the gallium atom but structural determination of $(TPP)In(SO_3CH_3)$ demonstrated that this complex is an *O,O′*-sulfonato intermolecular species in the solid state. The complex crystallizes as a one-dimensional polymer whose fundamental unit consists of two (TPP)In entities bridged by a sulfonato group.[207] This crystal structure was the first structural example of a polymeric metalloporphyrin. This study also presented the first demonstration that the ionic radii did not influence the out-of-plane distance of the metal. In fact, the polymeric association of $(TPP)In(SO_3CH_3)$ involves an ionic association between $[(TPP)In]^+$ and $[SO_3CH_3]^-$ ions.

The solid-state polymeric structural arrangement of $(TPP)In(SO_3CH_3)$ does not exist in solution. The presence of a nonoctahedral monomeric structure was demonstrated by ^1H NMR spectra of low-concentration solutions. However, aggregates similar to those in the solid state are formed at higher concentrations.[207]

Single-bonded complexes containing one porphyrin unit can be obtained by the reaction of metal carbonyls with σ-bonded metal–carbon porphyrins of OEP and TPP[209–211] (Scheme 29). The same compounds are also obtained when (P)InCl is allowed to react with the corresponding metal carbonyl monoanions.[209–211] Formation of a transient $(P)In\text{–}Fe(CO)_4\text{–}R$ species has been demonstrated as an intermediate in the synthesis of the trinuclear $[(P)In]_2Fe(CO)_4$ complex.[211] Formation of the inserted species proceeds via a mechanism similar to that for insertion of CO_2 into the metal–carbon bond of (P)In(R). This synthetic procedure for the metal–metal bonded derivatives is a classic route in organometallic chemistry and in theory can be applied to the synthesis of σ-bonded metal–carbon porphyrin com-

TABLE 3. Half-Wave Potentials (V vs SCE) for the Reversible First and Second Reductions of (P)MCl and (P)M(R) Where M = Ga, In, Tl, and Al in CH_2Cl_2 Containing 0.1 M TBA(PF_6)

	P = TPP								P = OEP			
	Ga[a]		In[b]		Tl[c]		Al[a]		Ga[a]	In[b]	Tl[c]	Al[d]
axial ligand	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	1st
$C(CH_3)_3$	-1.31	-1.74	-1.27	-1.71					-1.54	-1.54		
$CH(CH_3)_2$			-1.26	-1.67						-1.53		
C_4H_9	-1.29	-1.73	-1.26	-1.69			-1.19	-1.64	-1.53	-1.50		-1.48
C_2H_5	-1.27	-1.70	-1.25	-1.66					-1.51	-1.48		
CH_3	-1.29	-1.71	-1.24	-1.64	-1.27	-1.69	-1.18	-1.63	-1.53	-1.50	-1.52	-1.47
$C_2H_2C_6H_5$	-1.24	-1.67	-1.24	-1.64					-1.47	-1.48		
$C_2C_6H_5$	-1.19	-1.59						-1.49	-1.47	-1.49		
p-$OCH_3C_6H_4$					-1.25	-1.66	-1.14	-1.60			-1.49	-1.47
C_6H_5	-1.22	-1.66	-1.22	-1.62	-1.23	-1.64	-1.18	-1.60	-1.49	-1.47	-1.49	-1.47
C_6F_4H			-1.20	-1.60	-1.19	-1.60				-1.45	-1.43	
C_6F_5			-1.20	-1.60	-1.17	-1.58				-1.46	-1.42	
Cl^-	-1.16	-1.56	-1.09	-1.48	-0.91[e]				-1.41	-1.29	-1.19[e]	

[a] Reference 178. [b] References 179 and 180. [c] Reference 202b. [d] Reference 181. [e] E_{pc} measured at 0.10 V/s.

plexes with other central metals.

The photoinduced cleavage of a carbon–indium bond in (TPP)In(C_2H_5) has been reported.[212–216] Photoinduced homolytic cleavage of the indium–carbon bond produces a zwitterionic $TPP^-In(III)^+$ complex in which a positive charge is located on the indium atom and a negative one on the TPP ligand.[212] The photochemistry of this compound was studied by steady light and laser flash photolysis,[213] and the results demonstrate that the triplet state of (TPP)In(C_2H_5) is responsible for the photoreaction. This was ascertained on the basis of quantum yield and triplet decay measurements in the presence of ferrocene.[213]

B. Electrochemistry of Aluminum, Gallium, Indium, and Thallium σ-Bonded Complexes

The electrochemistry of group 13 σ-bonded metalloporphyrins has been reported by Kadish and Guilard.[178–181,202b] The reductions of (P)M(R) are reversible while oxidations of the same complexes are either reversible or irreversible, depending upon the specific central metal ion and specific σ-bonded R group.

Values of $E_{1/2}$ for the first reduction of complexes in the four different (P)M(R) series are summarized in Table 3. As seen in this table, $E_{1/2}$ values for reduction of a given (P)M(R) complex containing the same porphyrin ring and the same σ-bonded alkyl and aryl group shifts only slightly upon changing the central metal ion. For example, the reduction of (OEP)M(C_6H_5) in CH_2Cl_2 occurs at $E_{1/2} = -1.47$ V for M = Al[181] and In[180] and at $E_{1/2} = -1.42$ V for M = Ga[178] and Tl.[202b]

Each σ-bonded group 13 porphyrin undergoes an initial electroreduction at the porphyrin π ring system. However, the mechanism for electroreduction of (P)-Tl(R) is not as simple as for the other three series of group 13 complexes. A two-electron reduction of the Tl(III) metal to give a Tl(I) species may occur for (P)Tl(R).[202b] However, the similarity in $E_{1/2}$ values for reduction of all complexes in the four related (P)M(R) series (see Table 3) suggests that reduction of (P)Tl(R) is similar to the other complexes in that the electrode reaction initially involves an addition of one electron to the porphyrin π ring system.

Electrooxidation of a given σ-bonded group 13 complex leads to one, two, or three voltammetric peaks, depending upon the specific central metal ion, the specific R group, and the specific solvent system. Each (P)Al(R), (P)Ga(R), or (P)In(R) complex, where R is an alkyl group, undergoes an electrochemically reversible one-electron oxidation, which is followed by rapid cleavage of the metal–carbon bond (eq 47). This results

$$(P)M(R) \overset{-e^-}{\rightleftharpoons} [(P)M(R)]^{\bullet +} \rightarrow [(P)M]^+ + R^\bullet \qquad (47)$$

in an overall irreversible oxidation process and a peak potential, E_p, that ranges between 0.64 and 1.06 V, depending upon the nature of the alkyl group, the specific porphyrin ring (OEP or TPP), and the potential scan rate. The electrogenerated $[(P)M]^+$ is also electroactive and well-defined oxidations for these ionic porphyrins are monitored at more positive potentials.[178,179,181]

Reversible oxidations are also obtained for (P)In(R) and (P)Ga(R) complexes with specific σ-bonded axial ligands. (P)Ga($C_2C_6H_5$)[178] and (P)In($C_2C_6H_5$),[179] as well as (P)In(C_6F_4H) and (P)In(C_6F_5),[180] undergo reversible oxidations at the porphyrin π ring system. Likewise, all of the (P)Tl(R) complexes that have been investigated to date can be reversibly oxidized by two electrons without cleavage of the thallium–carbon bond on the time scale of cyclic voltammetry.[202b]

VII. Silicon, Germanium, and Tin

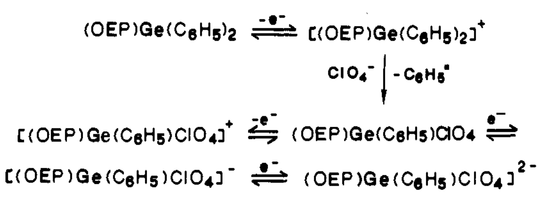
A. Synthesis and Reactivity

Group 14 σ-bonded metalloporphyrins have been synthesized from the reaction of (P)MCl_2 with Grignard reagents or with alkyl- or aryllithium. The preparation of dialkyl or diaryl silicon,[217] germanium,[218–226] and tin[224,225,227] complexes has been described. However, the yields are generally poor because the complexes are light sensitive and are readily oxidized.

(TPP)Ge$(R)_2$, where R = CH_3, n-C_3H_7, n-C_8H_{17}, and C_6H_5, were first synthesized from (TPP)$GeCl_2$ as NMR shift reagents.[220,221] Later, other (TPP)M$(R)_2$ complexes were synthesized by treating (TPP)MCl_2 with RMgX, where M = Ge and R = C_2H_5, n-C_3H_7, n-C_4H_9, i-C_4H_9, $CH_2Si(CH_3)_3$, $CH_2CH{=}CH_2$, or n-C_6H_{13} or where M = Sn and R = C_2H_5 or $CH_2Si(CH_3)_3$.[224,225,227] Most of these complexes have only been characterized in solution.

The alkylation of (P)Sn$(OH)_2$ by Grignard reagents where P = TPP, TPC, or TPiBC gave (dialkylstannyl)isobacteriochlorins.[227] The presence of a transition-metal impurity in the Grignard reagent led to

SCHEME 30



reduction of the macrocycle rather than toward tin alkylation of TPP and TPC.[227] This suggests a one-electron-transfer mechanism when the macrocycle is alkylated by Grignard reagents.

The synthesis and characterization of (OEP)Ge$(C_6H_5)_2$ and (OEP)Ge(C_6H_5)Cl have also been reported.[226] The latter complex was isolated from photodecomposition of the former species and is the first example of an isolated group 14 metalloporphyrin that contains only one σ-bonded ligand. The mechanism for formation of (OEP)Ge(C_6H_5)Cl from (OEP)Ge$(C_6H_5)_2$ in $CHCl_3$ undoubtedly involves radical attack and Cl• abstraction from $CHCl_3$ after loss of one phenyl group.

Two silicon-carbon σ-bonded complexes, (OEP)Si$(CH_3)_2$ and (OEP)Si$(C_6H_5)_2$, have been prepared according to the Grignard method.[217] These compounds were isolated as solid samples but both are photoactive and O_2 sensitive in solution and are thus readily decomposed.

Some aspects of germanium and tin porphyrin chemical reactivity have been reported. These compounds are readily oxidized by oxygen in solution and in the presence of light to give peroxides.[224] It was suggested that the first step of the reaction is fast and gives a monoperoxide whereas the second step is slow and leads to a diperoxide (eq 48).

$$(TPP)M(R)_2 \xrightarrow[\text{fast}]{O_2,\ h\nu} (TPP)M(OOR)(R) \xrightarrow[\text{slow}]{O_2,\ h\nu} (TPP)M(OOR)_2 \quad (48)$$

$$M = Ge, Sn$$

Pure samples of monoperoxides have been prepared[228] by using selected wavelengths and temperatures for the photooxidation of (TPP)M$(R)_2$ where M = Ge and R = C_2H_5, n-C_3H_7, n-C_4H_9, i-C_4H_9, CH_2SiMe_3, $CH_2{=}CH\text{-}CH_2$, $C_6H_5CH_2$, n-C_6H_{13}, or i-C_3H_7 and where M = Sn and R = $CH_2Si(CH_3)_3$.[228] The monoperoxides were characterized on the basis of ^{1}H NMR and UV-visible data.

Miyamoto and co-workers[127] demonstrated that rats fed with (MGP)Ge$(CH_3)_2$ (MGP = 5,10,15,20-tetrakis-[3,5-bis(1,1-dimethylethyl)phenyl]porphinato had fewer solid tumors than those not fed with this compound. The compound also showed considerable activity toward neoplastic tissues both in vitro and in vivo, which suggests that activation of the methyl groups attached to the germanium atom might play a significant role in the anticancer drug action.

B. Electrochemistry of Germanium and Silicon Porphyrins

The electrochemistry of Ge(IV) and Si(IV) porphyrins with σ-bonded alkyl and aryl groups has been reported by Kadish and Guilard.[217,219,226] Each electrode reaction was investigated in the dark and in the strict absence of O_2. An insertion of O_2 into the germanium-carbon bond of (P)Ge$(R)_2$ was postulated to occur,[228] but later studies[217,226] showed that these reactions are more complicated than initially suggested.

The electroreduction of (P)Ge$(R)_2$[226] or (P)Si$(R)_2$[217] occurs in one or two single-electron-transfer steps, depending upon the porphyrin macrocycle. $E_{1/2}$ values range between −1.40 and −1.58 V for the first reduction of (OEP)Ge$(R)_2$[226] and (OEP)Si$(R)_2$[217] in PhCN. No second reduction is observed for the OEP derivatives in this solvent. In contrast, (TPP)Ge$(C_6H_5)_2$ and (TPP)Ge$(CH_2C_6H_5)_2$ are reduced via two one-electron-transfer steps, which in PhCN occur at $E_{1/2}$ = −1.10 and −1.65 V.[226]

The cleavage of one σ-bonded phenyl group from the germanium ion of electrogenerated $[(OEP)Ge(C_6H_5)_2]^+$ is rapid and leads to (OEP)Ge$(C_6H_5)ClO_4$, which undergoes the series of oxidations and reductions shown in Scheme 30.

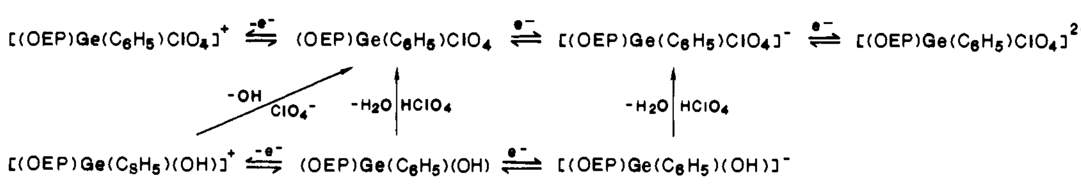
Similar types of reactions occur for other (P)Ge$(R)_2$[226] and (P)Si$(R)_2$[217] derivatives and in all cases the final product after electrooxidation has been identified as (P)Ge(R)X or (P)Si(R)X, where X = ClO_4^-, Cl^-, or OH^-.

(P)Ge(R)Cl can also be generated from (P)Ge$(R)_2$ in degassed $CHCl_3$ solutions by illumination with visible light.[226] Electrochemical oxidation of (OEP)Ge(C_6H_5)OH or (OEP)Ge(C_6H_5)Cl gives the same product, which was spectroscopically and electrochemically identified as (OEP)Ge$(C_6H_5)ClO_4$.[226]

The electrochemically initiated conversion of (P)Ge$(R)_2$ to (P)Ge(R)X or (P)Si$(R)_2$ to (P)Si(R)X provides an excellent electrosynthetic method for obtaining group 14 metalloporphyrins that contain one σ-bonded ligand and one ionic ligand. In this regard, a number of (P)Ge(R)X and (P)Si(R)X derivatives have been synthesized and characterized, both spectroscopically and electrochemically.[217,226]

Electrochemically or photochemically synthesized (OEP)Ge$(C_6H_5)ClO_4$ undergoes two reductions at $E_{1/2}$ = −0.82 and −1.30 V in PhCN, 0.1 M TBAP. The complex also undergoes a single reversible oxidation at $E_{1/2}$ = 1.40 V. (OEP)Ge$(C_6H_5)ClO_4$ can be converted to (OEP)Ge(C_6H_5)OH either by electroreduction or by titration with TBA(OH) while (OEP)Ge(C_6H_5)OH can be converted to (OEP)Ge$(C_6H_5)ClO_4$ either by electrooxidation or by titration with $HClO_4$. These reactions are given in Scheme 31 for the case of (OEP)Ge-

SCHEME 31



$(C_6H_5)X$. The same types of chemical and electrochemical reactions are observed for (P)Ge(R)X and (P)Si(R)X.

The electrochemistry of $(P)Ge(C_6H_5)(Fc)$ and $(P)Ge(Fc)_2$, where P is the dianion of octaethylporphyrin or tetraphenylporphyrin and Fc is a ferrocenyl group, has also been reported.[218,219] The former series of complexes provides the first synthetic examples of metalloporphyrins that contain two different σ-bonded axial groups.

The physicochemical properties of neutral $(P)Ge(Fc)_2$ and $(P)Ge(C_6H_5)(Fc)$ are similar to other σ-bonded $(P)Ge(R)_2$ derivatives since both groups contain two germanium–carbon σ bonds. However, the magnitude of the Soret band molar absorptivities for $(P)Ge(Fc)_2$ and $(P)Ge(C_6H_5)(Fc)$ are only about half that of other $(P)Ge(R)_2$ complexes, and this was attributed to a delocalization of electron density from the porphyrin macrocycle onto the ferrocenyl group.[218,219] In addition, the germanium–carbon σ bonds in $(P)Ge(Fc)_2$ and $(P)Ge(C_6H_5)(Fc)$ are much more stable than in other $(P)Ge(R)_2$ complexes.

The first and second oxidations of $(P)Ge(Fc)_2$ and $(P)Ge(C_6H_5)(Fc)$ are assigned as electron abstractions from the σ-bonded Fc ligand. The third oxidation occurs at the porphyrin π ring system. On the basis of a similarity between $(P)Ge(Fc)_2$ and other biferrocene derivatives, an interaction between two iron centers of $(P)Ge(Fc)_2$ was deduced.[218,219]

VIII. Other Metal σ- or π-Bonded Porphyrins

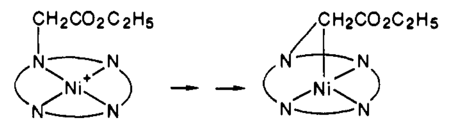
This section describes metal σ- or π-bonded porphyrins that are not described in the previous sections. These include the derivatives of Ti, Mo, Ni, and Zn.

Reaction of the low-valent (TPP)TiF complex with Grignard reagents gives σ-bonded (TPP)Ti(R) derivatives, where R is C_6H_5, $CH_2C_6H_5$, or p-$CH_3C_6H_4$.[229] Each compound exhibits a nine-line ESR spectrum, reflecting interaction of the unpaired electron with the four equivalent nitrogen nuclei of the porphyrin macrocycle. A six-coordinate (TPP)Ti(R)(L) species is not formed by addition of ligands such as toluene, *N*-methylimidazole, or THF to (TPP)Ti(R). This is in contrast to (TPP)TiF. Autoxidation of (TPP)Ti(R) generates (TPP)Ti(O) and R–R via the transient formation of the $(TPP)Ti(O_2)$ peroxide species.[229]

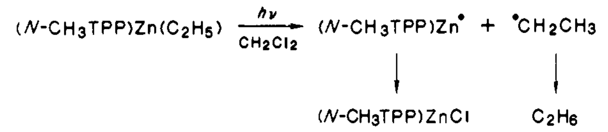
Both π- and σ-bonded molybdenum porphyrin complexes are known. Reduction of $(TPP)MoCl_2$ by $LiAlH_4$ in the presence of diphenylacetylene gives (TPP)Mo(PhC≡CPh).[102] The distance between the Mo(II) atom and the acetylenic carbon atoms proves that the acetylene ligand acts as a four-electron donor. The σ-bonded $(TPP)Mo(C_6H_5)Cl$ complex is synthesized by photodecomposition of $(TPP)Mo(CO)_2$ in benzene containing chlorinated impurities.[230] It was suggested that the six-coordinate $(TPP)Mo(C_6H_5)Cl$ derivative is formed via a transient (TPP)Mo species that leads to $(TPP)Mo(C_6H_5)H$. However, if chloride is present in the reaction mixture, a substitution of the hydride ligand will occur.

As shown for Co porphyrin complexes in section V, a coordination with the central metal of the metalloporphyrin is not the one and only geometrical choice available to a carbene fragment. The carbene may also be inserted into a metal–nitrogen bond, and this type of complex has been isolated in the nickel series. Reaction of $[(N\text{-}CHCO_2C_2H_5)TPP)Ni]^+ClO_4^-$ with base first yields an aziridine complex but after longer periods, this derivative disappears as the $(TPP)Ni(CHCO_2C_2H_5)$ carbene complex is formed[231,232] (Scheme 32).

SCHEME 32



SCHEME 33



A structure of the d^8 $(TPP)Ni(CHCO_2C_2H_5)$ complex has been determined.[232,233] The nickel atom is tetracoordinated with the carbon of the $CHCO_2C_2H_5$ carbene group and with the three nitrogen atoms of the macrocycle. This was demonstrated[139] for the $[(OEP)Co(CHCO_2C_2H_5)]Cl$ complex. It is remarkable to note that the Ni–C bond length of 1.905 Å is close to that expected for a pure σ bond (1.92 Å).

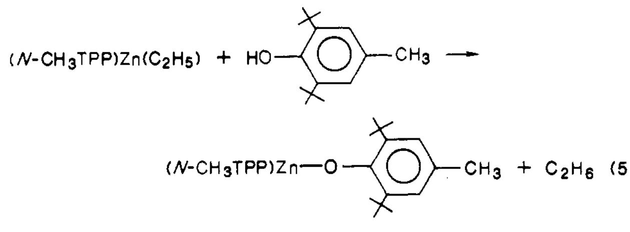
The reaction of free base *N*-methyl-substituted tetraphenylporphyrin ($(N\text{-}CH_3TPP)H$) with diethylzinc ($Zn(C_2H_5)_2$) gives σ-bonded $(N\text{-}CH_3TPP)Zn(C_2H_5)$ according to eq 49.[234] The final complex is stable under

$$(N\text{-}CH_3TPP)H + Zn(C_2H_5)_2 \rightarrow (N\text{-}CH_3TPP)Zn(C_2H_5) + C_2H_6 \quad (49)$$

anaerobic conditions in the dark but is decomposed by irradiation with visible light in solution (Scheme 33).[235] $(N\text{-}CH_3TPP)Zn(CH_2CH_3)$ reacts with carbon dioxide in the presence of a secondary amine or alcohol, and this results in the formation of $(N\text{-}CH_3TPP)Zn(O_2CX)$, where X = NR_2 and R = C_2H_5, *n*-C_3H_7, *i*-C_3H_7, or *i*-C_4H_9 or where X = C_2H_5, *i*-C_3H_7, or *t*-C_4H_9 (eq 50). It has also been shown that the reaction of CO_2 with $(N\text{-}CH_3TPP)Zn(C_2H_5)$ in the presence of amine or alcohol is considerably accelerated.

$$(N\text{-}CH_3TPP)Zn(C_2H_5) + HX + CO_2 \rightarrow (N\text{-}CH_3TPP)Zn(O_2CX) + C_2H_6 \quad (50)$$

Finally, substitution reactions of $(N\text{-}CH_3TPP)Zn(C_2H_5)$ with hindered phenols in benzene are accelerated dramatically by irradiation with visible light and lead to the formation of metalloporphyrins that have the corresponding phenoxy group bonded to the zinc metal of the metalloporphyrin[158] (eq 51)


(51)

IX. Summary

This review has discussed the synthesis, chemical reactions, and electrochemical behavior of metal–carbon bonded metalloporphyrins. The initial studies on metal–carbon bonded complexes were published over 20 years ago. However, the field is still relatively new and the majority of work results from studies carried out during the past 3 years. The field of organometallic porphyrin chemistry is rapidly expanding and future synthetic developments should lead to new complexes possessing novel metal–carbon interactions and novel reactivity. There is no doubt that these types of complexes are of interest in modeling several important biological processes, in expanding the field of synthetic organometallic chemistry, and in the preparation of new polymeric materials for use as conducting properties.

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X. Abbreviations Used for Axial Ligands and Other Species

P	unspecified porphyrin
C_{12}TPP	C_{12} "basket handle" porphyrin
TPC	5,10,15,20-tetraphenylchlorin
TPiBC	5,10,15,20-tetraphenylisobacteriochlorin
Et	ethyl
$n\text{-}C_3H_7$	*n*-propyl
$i\text{-}C_3H_7$	isopropyl
$n\text{-}C_4H_9$	*n*-butyl
$i\text{-}C_4H_9$	isobutyl
$t\text{-}C_4H_9$	*tert*-butyl
$n\text{-}C_5H_{11}$	*n*-pentyl
$n\text{-}C_6H_{13}$	*n*-hexyl
$n\text{-}C_8H_{17}$	*n*-octyl
C_8H_{13}	*cis*-bicyclo[3.3.0]oct-1-yl
$CH{=}CHC_6H_5$	styryl
$c\text{-}C_6H_{11}$	cyclohexyl
$C_2C_6H_5$	phenylacetylenyl
N-R	*N*-alkyl or *N*-aryl
$N\text{-}C_6H_5$	*N*-phenyl
$n\text{-}BuS^-$	*n*-butylthiolate
C_6F_4H	2,3,5,6-tetrafluorophenyl
C_6F_5	pentafluorophenyl
$m\text{-}CH_3$	*m*-methyl
$p\text{-}CH_3$	*p*-methyl
$p\text{-}OCH_3$	*p*-methoxy
$p\text{-}CF_3$	*p*-trifluoromethyl
$p\text{-}Et_2N$	*p*-diethylamino
M	mesityl
Fc	ferrocenyl
TBA(ClO_4^-)	tetrabutylammonium perchlorate
TBA(PF_6)	tetrabutylammonium hexafluorophosphate
N-MeIm	*N*-methylimidazole
py	pyridine
PhCN	benzonitrile
DMF	dimethylformamide
THF	tetrahydrofuran
Me_2SO	dimethyl sulfoxide
P^{Me}	$CH_2CH_2COOOCH_3$
P^H	CH_2CH_2COOH
TEMPO	3,3,6,6-tetramethylpiperidineoxy

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