

The Organometallic Chemistry of Transition-Metal Porphyrin Complexes[†]

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Metalloporphyrin chemistry has become a crossroads linking the traditional fields of organometallic and coordination chemistry.^{1a} Surprises abound in the context of novel complexes, of unanticipated radical mechanisms for classic organometallic reactions, and of redox-induced migrations by carbon substituents between the metal and the pyrrolic nitrogens. These migrations are significant in establishing another link between organometallic chemistry and naturally existing processes, a role previously held by vitamin B₁₂ alone.

Some of these unusual properties derive from special structural features of the porphyrin ligand. The four planar nitrogen ligands usually restrict axial substituents to mutually trans positions; powerful trans-labilizing effects are evident. In the absence of trans ligands, strong metal-carbon bonds are present,^{1d} and for the 4d and 5d metal porphyrin complexes multiple metal-metal bonds occur.^{1b,c} The frontier orbitals of the macrocycle and the metal have similar energies so that the redox properties of the porphyrin π -electrons and the metal d orbitals may become entwined. Finally, coordination geometries other than residing in the porphyrin "hole" are available to some metals, forming out-of-plane complexes.

Metalloporphyrin compounds are known for all of the transition metals, the lanthanides, and many of the actinides and main-group elements. Most organometallic porphyrin species involve the transition metals, especially the iron and cobalt triads. Herein we emphasize the synthesis of representative organotransition metal compounds and recent studies of unusual reaction mechanisms.

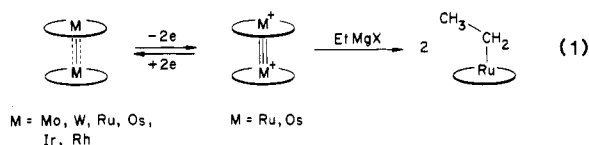
Synthesis and Physical Properties

σ -Bonded Complexes. Transition-metal porphyrin complexes having metal-carbon σ -bonds are usually prepared by metathetical reactions. For example, Grignard reagents and organolithium compounds react with first row halides M(Por)X (M = Co, Fe) producing a wide range of alkyl, aryl, and vinyl derivatives, M-

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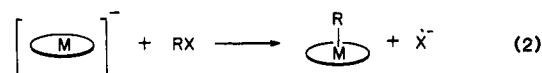
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(Por)R.²⁻⁵ An exceptional variation of this scheme involves reaction between the ethyl Grignard reagent and the ruthenium(III) dimer, [Ru(OEP)]₂²⁺ (which is produced by oxidation of the neutral dimer) (eq 1).^{1e}



This may become a general synthetic route to ruthenium(III) porphyrin alkyls. As we shall see below, the metalloporphyrin dimers of the heavier elements are of great synthetic utility.

Reactions of the opposite polarity are also well-known. The highly nucleophilic metal(I) porphyrin anions (M = Fe, Co, Rh, and Ir) react with halides to form metal(III) porphyrin alkyls (eq 2).^{2,4,6,7} Stereo-



chemical and kinetic studies have provided evidence for the S_N2 character of these metal alkylations.^{6a,7} Iron(I)

[†]Porphyrin ligands are abbreviated as follows: Por, porphyrinato dianion unspecified; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; TPP, 5,10,15,20-tetraphenylporphyrinato dianion; TTP, 5,10,15,20-tetra-*p*-tolylporphyrinato dianion; PPIX, dianion of protoporphyrin IX dimethyl ester; *N*-RPor, *N*-alkylporphyrin anion. Other abbreviations: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Ph, phenyl; R, alkyl group; Ar, aryl group; X, halide; THF, tetrahydrofuran; py, pyridine.

(1) (a) A more detailed version of the present paper can be consulted for further discussion and literature citations: Brothers, P. J., Ph.D. Thesis, Stanford University, May 1985. (b) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* 1983, 80, 7684-7688. (c) Collman, J. P.; Prodoliet, J. W.; Leidner, C. R. *J. Am. Chem. Soc.* 1986, 108, 2916-2921. (d) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E. *J. Am. Chem. Soc.* 1985, 107, 6110-6111, and references therein. (e) Collman, J. P.; Prodoliet, J.; Leidner, C. R.; McElwee-White, L.; Rose, E., unpublished results.

(2) Clarke, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc. C* 1968, 881-885, and references therein.

(3) (a) Cocolios, P.; Lagrange, G.; Guillard, R. *J. Organomet. Chem.* 1983, 253, 65-79, and references therein. (b) Ogoshi, H.; Sugimoto, H.; Yoshida, Z.-I.; Kobayashi, H.; Sakai, H.; Maeda, Y. *J. Organomet. Chem.* 1982, 224, 185-195. (c) Battioni, J.-P.; Lexa, D.; McElwee-White, L.; Savéant, J.-M. *J. Am. Chem. Soc.* 1983, 105, 207-215.

(4) (a) Ogoshi, H.; Setsune, J.-I.; Omura, T.; Yoshida, Z.-I. *J. Am. Chem. Soc.* 1975, 97, 6461-6466, and references therein. (b) Ogoshi, H.; Watanabe, E.-I.; Koketzu, N.; Yoshida, Z.-I. *J. Chem. Soc., Chem. Commun.* 1974, 943-944, and references therein. (c) Ogoshi, H.; Setsune, J.-I.; Yoshida, Z.-I. *J. Organomet. Chem.* 1978, 159, 317-328.

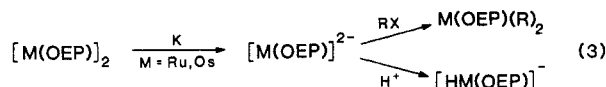
(5) Callot, H. J.; Metz, F. *J. Chem. Soc., Chem. Commun.* 1982, 947-948, and references therein.

(6) (a) Perrée-Fauvet, M.; Gaudemer, A.; Boucly, P.; Devynck, J. J. *J. Organomet. Chem.* 1976, 120, 439-451. (b) Ogoshi, H.; Setsune, J.-I.; Yoshida, Z.-I. *J. Organomet. Chem.* 1980, 185, 95-104. (c) Clarke, D. A.; Grigg, R.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc., Chem. Commun.* 1967, 309-310. (d) Lagrange, G.; Cocolios, P.; Guillard, R. *J. Organomet. Chem.* 1984, 260, C16-C20.

(7) Lexa, D.; Mispelter, J.; Savéant, J.-M. *J. Am. Chem. Soc.* 1981, 103, 6806-6812.

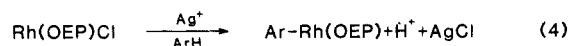
porphyrin anions, generated electrochemically, even react with aryl and vinyl halides;⁸ cobalt and rhodium porphyrin anions react with ethylene oxide, aziridine, methyl acrylate, acrylonitrile, and phenylacetylene to produce metal-carbon σ -bonded species.^{4a,6b} Even carbon-carbon bonds in strained carbocyclic rings can be ruptured by these potent metal anions, affording organometallic porphyrin derivatives. For example, cyclopropane rings bearing electron-withdrawing groups form γ -substituted alkyl cobalt and rhodium complexes.^{6b} Even the unactivated rings in nortricyclanone, quadricyclane, and bicyclobutane react with $[\text{Rh}(\text{OEP})]^-$, forming well-characterized organorhodium species.^{6b} Such chemistry is not limited to the formation of metal-carbon bonds. The rhodium anion has been used to prepare the novel heterobimetallic dimer $\text{Rh}(\text{OEP})\text{-In}(\text{OEP})$ by reaction with $\text{In}(\text{OEP})\text{Cl}$.⁹

The situation with ruthenium and osmium porphyrins is different; few $\text{M}(\text{III})$ halide derivatives are known^{10,11} and the $\text{Ru}(\text{I})$ and $\text{Os}(\text{I})$ monoanions are presently unknown. However, the $\text{M}(\text{0})$ dianions, generated by reduction of the metal-metal bonded dimers, are very useful synthons metal(III) be either alkylated or monoprotonated (eq 3).^{1d,12,13} The iron(0) dianion,



$[\text{Fe}(\text{TPP})]^{2-}$, is also known, but the reaction chemistry has been little studied.¹⁴

An alternative method for preparing organometallic porphyrin derivatives is electrophilic substitution; thus far this has been most studied with rhodium porphyrins. For example, treatment of $\text{Rh}(\text{OEP})\text{Cl}$ with silver salts in the presence of an arene (PhH , PhOMe , PhMe , PhCl) results in the formation of para-substituted rhodium aryls¹⁵ (eq 4). The aromatic substitution



pattern (only para), the failure of oxygen to inhibit the reaction, the noninvolvement of the weak C-H bonds in toluene and anisole, and the relative arene reactivities are all consistent with electrophilic aromatic substitution by $[\text{Rh}(\text{OEP})]^+$. The chloride, $\text{Rh}(\text{OEP})\text{Cl}(\text{H}_2\text{O})$, is itself sufficiently electrophilic to form organorhodium species with ethyl vinyl ether and various acetylenes.^{16a} Although a possibly related reaction has been reported for $\text{Co}(\text{OEP})$,^{16b} this technique has not yet been applied

(8) Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1982**, *104*, 3503-3504.

(9) Jones, N. L.; Carroll, P. J.; Wayland, B. B. *Organometallics* **1986**, *5*, 33-37.

(10) Barley, M.; Becker, J. Y.; Domazetis, G.; Dolphin, D.; James, B. R. *Can. J. Chem.* **1983**, *61*, 2389-2396.

(11) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151-5163.

(12) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570-4571, and references therein.

(13) Collman, J. P.; McElwee-White, L.; Brothers, P. J.; Rose, E., *J. Am. Chem. Soc.* **1986**, *108*, 1332-1333, and references therein.

(14) (a) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E., unpublished results. (b) Mashiko, T.; Reed, C. A.; Haller, K. J.; Scheidt, W. R. *Inorg. Chem.* **1984**, *23*, 3192-3196.

(15) Aoyama, Y.; Yoshida, T.; Sakurai, K.-I.; Ogoshi, H. *Organometallics* **1986**, *5*, 168-173.

(16) (a) Ogoshi, H.; Setsune, J.-I.; Nanbo, Y.; Yoshida, Z.-I. *J. Organomet. Chem.* **1978**, *159*, 329-339. (b) Sugimoto, H.; Nagano, M.; Yoshida, Z.-I.; Ogoshi, H. *Chem. Lett.* **1980**, 521-524.

to other metalloporphyrins.

The d^6 σ -bonded alkyl and aryl complexes of Co, Rh, and Ir are diamagnetic, air stable species with well-resolved ^1H NMR spectra. Both these and the analogous iron complexes can coordinate a sixth ligand in the vacant axial site.^{3,6a,6d,17,18} The porphyrin ring current imparts large upfield chemical shifts to axial substituents; for example $[\text{M}(\text{Por})\text{H}]^-$ ($\text{M} = \text{Ru}, \text{Os}$)^{1d} and the isoelectronic $\text{Rh}(\text{OEP})\text{H}$ ¹⁹ species exhibit hydride resonances between -33 and -66 ppm. Surprisingly, the six-coordinate d^4 dialkyls $\text{M}(\text{Por})\text{R}_2$ ($\text{M} = \text{Ru}, \text{Os}$), are diamagnetic as evidenced by sharp, temperature-independent ^1H NMR spectra.^{1d} The paramagnetic iron(III) porphyrin alkyl, aryl, and vinyl complexes are low-spin ($S = 1/2$) complexes in contrast to the structurally analogous high-spin ($S = 5/2$) halide species $\text{Fe}(\text{Por})\text{-X}$.^{3,7} The low-spin $\text{Fe}(\text{Por})\text{R}$ complexes exhibit more negative $\text{Fe}(\text{III}/\text{II})$ redox couples and are thus much more difficult to reduce than are their high-spin analogues.

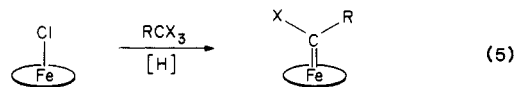
The ^1H NMR spectra of the paramagnetic organoiron complexes exhibit contact shifted signals for porphyrin substituents; protons on the α - or β -carbons of the alkyl group are obscured by line broadening but γ -protons can be observed.^{3a,7}

Metal-alkyl bonds in porphyrin complexes are subject to homolysis, which can be reversible. Further on we shall see the importance of such radical processes. Methyl radicals are readily captured by iron(II) porphyrins forming $\text{Fe}(\text{Por})(\text{CH}_3)$; however, chloromethyl radicals are slower to undergo this reaction. The latter property has been suggested as a possible cause for the toxicity of chloromethyl-containing compounds.²⁰

The Co-C bond in organocobalt(III) porphyrins is photochemically labile.² Much of the interest in such compounds stems from their potential as models for vitamin B₁₂; however, this analogy is weak.²¹

Carbene Complexes. Several metalloporphyrin carbene complexes are known, but these are presently limited to the iron triad. The carbene carbons bear at least one substituent other than hydrogen. The unsubstituted carbene complexes are unstable with respect to olefin formation.^{1d,12} These diamagnetic complexes $\text{M}(\text{Por})(\text{CR}_2)$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) have a formal $\text{M}(\text{II})$ oxidation state and exhibit a capacity to bind a trans axial ligand (py , ROH , etc.).²² The air sensitivity of these species depends on the carbene substituents.

Mansuy first showed that reaction between an iron porphyrin and RCX_3 ($\text{X} = \text{Cl}, \text{Br}$) in the presence of a reducing agent (Fe powder or sodium dithionite) is a general method for preparing iron porphyrin carbene complexes (eq 5). Carbene complexes, $\text{Fe}(\text{TPP})(\text{CXR})$



(17) Lançon, D.; Cocolios, P.; Guillard, R.; Kadish, K. M. *Organometallics* **1984**, *3*, 1164-1170.

(18) Lançon, D.; Cocolios, P.; Guillard, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 4472-4478.

(19) Setsune, J.-I.; Yoshida, Z.-I.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983-987.

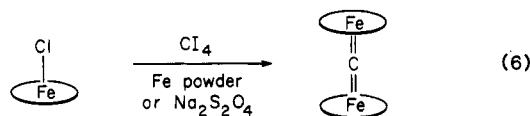
(20) Brault, D.; Neta, P. *J. Am. Chem. Soc.* **1981**, *103*, 2705-2710, and references therein.

(21) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.* **1979**, *100*, 159-172.

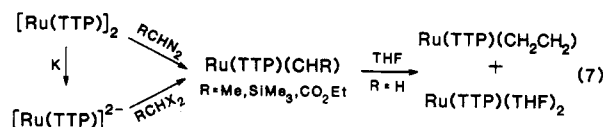
(22) Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681-690, and references therein.

having either electron-withdrawing ($R = \text{CN}, \text{CO}_2\text{Et}$) or electron-releasing substituents ($R = \text{Me}, \text{CH}_2\text{OH}$, etc.) have been characterized.^{22,23} The dichlorocarbene complex, $\text{Fe}(\text{TTP})(\text{CCl}_2)(\text{H}_2\text{O})$, prepared from CCl_4 was studied by X-ray diffraction.²² It is a useful synthetic intermediate, for example, forming isocyanide complexes upon reaction with primary amines. The short bond length (1.83 Å) is consistent with an Fe–C double bond.

The analogous dibromocarbene was prepared similarly from CBr_4 ; however, Cl_4 afforded a novel μ -carbido complex $[\text{Fe}(\text{TTP})]_2\text{C}$ which can be considered a "double carbene" (eq 6).^{24,25}



Ruthenium and osmium porphyrin carbene complexes have been prepared, either from treatment of the dianion with a geminal dihalide or by reaction of the metal-metal bonded dimers with diazoalkanes (eq 7).^{1d,12,26} These carbene complexes are unusual in



having a hydrogen substituent; however, the putative methylene complex spontaneously decomposes to form the unprecedented ethylene complex $\text{Ru}(\text{TTP})(\text{CH}_2\text{CH}_2)$. Such olefin forming reactions are well-known for unhindered methylene complexes.²⁷

The axial symmetry of the porphyrin ring as observed by ^1H NMR is retained for both the iron and ruthenium complexes.^{1d,12,22} This indicates that at ambient temperatures there is no barrier to rotation of the carbene ligand. In fact, an electronic barrier to rotation would not be expected, since the M–C π -bond involves the symmetry-equivalent d_{xz} and d_{yz} orbitals of the metalloporphyrin fragment.

Some of the interest in iron porphyrin carbenes derives from the formal analogy between these species and iron oxo complexes believed to be the active intermediates in enzymes such as catalases, peroxidases, and cytochrome P-450.²⁸ A related high-spin iron nitrene complex $(\text{TPP})\text{Fe}=\text{N}-\text{NR}_2$ has also been prepared and structurally characterized.²⁹ In spite of some spectroscopic similarities, the three structurally related species, oxo, nitrene, and carbene, are not particularly comparable and undoubtedly manifest different re-

activity patterns. It is interesting that both singly and doubly bonded iron-carbon intermediates are thought to be formed during the metabolism of certain substrates by cytochrome P-450. For example, P-450 metabolites of the anaesthetic halothane³⁰ and the insecticide benzodioxole³¹ may be iron porphyrin carbene complexes.

π -Complexes. Only two metalloporphyrin π -complexes, where bonding results from interactions between metal d orbitals and the π or π^* orbitals of an unsaturated ligand, have been reported. The ruthenium dimer $[\text{Ru}(\text{TTP})]_2$ is cleaved upon treatment with ethylene in THF solution to produce the robust ethylene complex $\text{Ru}(\text{TTP})(\text{CH}_2\text{CH}_2)$.¹² The ethylene ligand gives rise to a singlet at –4 ppm in the ^1H NMR spectrum. The same species and the osmium congener also result from the reaction of the dianions $[\text{M}(\text{TTP})]^{2-}$ with 1,2-dibromoethane.^{1d,12}

Reduction of $\text{Mo}^{\text{IV}}(\text{TPP})\text{Cl}_2$ by LiAlH_4 in the presence of excess diphenylacetylene results in a molybdenum(II) complex with a single coordinated diphenylacetylene ligand. An X-ray crystal structure determination of $\text{Mo}(\text{TPP})(\text{PhC}\equiv\text{CPh})$ demonstrated that the Mo–C distances are the shortest ever observed for a molybdenum acetylene complex and indicated that the acetylene ligand is a four-electron donor.³²

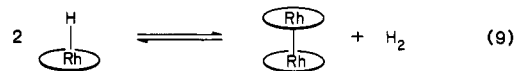
Free-Radical Processes

One of the most remarkable features of porphyrin organometallic chemistry is that in the absence of readily available cis coordination sites, alternate mechanisms have emerged by which familiar transformations such as insertion, and α - and β -elimination take place. These new processes involve novel free-radical pathways that are unprecedented in organometallic chemistry.

Consider, for example, the apparent insertion of CO into the Rh–H bond of $\text{Rh}(\text{OEP})\text{H}$ to produce a formyl species (eq 8).³³ This remarkable process, the only



example of an equilibrium between a metal hydride and CO where the formyl product is thermally favored, was discovered by Wayland and co-workers. The mechanism was subsequently shown by Halpern to be a radical chain process.³⁴ The key to this is the equilibrium shown in eq 9, wherein catalytic amounts of the rhodium dimer are formed from the hydride. Homolytic dissociation of the dimer yields the chain-carrying $\bullet\text{Rh}(\text{OEP})$ fragment (eq 10–12).



Initiation/Termination:



(23) (a) Mansuy, D.; Guerin, P.; Chottard, J. C. *J. Organomet. Chem.* **1979**, *171*, 195–201. (b) Guerin, P.; Battioni, J.-P.; Chottard, J.-C.; Mansuy, D. *J. Organomet. Chem.* **1981**, *218*, 201–209.

(24) Mansuy, D.; Lecomte, J.-P.; Chottard, J.-C.; Bartoli, J.-F. *Inorg. Chem.* **1981**, *20*, 3119–3121. This compound is the subject of a theoretical study.²⁵

(25) Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328–3341.

(26) Collman, J. P.; Brothers, P. J.; Leidner, C. R., unpublished results.

(27) (a) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811–5819. (b) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577–6578.

(28) Mansuy, D.; Chottard, J.-C.; Lange, M.; Battioni, J.-P. *J. Mol. Catal.* **1980**, *7*, 215–226.

(29) Mahy, J. P.; Battioni, P.; Mansuy, D.; Fischer, J.; Weiss, R.; Mispelter, J.; Morgenstern-Badarau, I.; Gans, P. *J. Am. Chem. Soc.* **1984**, *106*, 1699–1706.

(30) Mansuy, D.; Battioni, J.-P.; *J. Chem. Soc., Chem. Commun.* **1982**, 638–639.

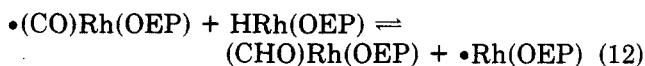
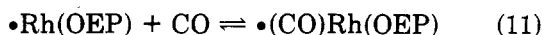
(31) Mansuy, D.; Battioni, J.-P.; Chottard, J.-C.; Ullrich, V. *J. Am. Chem. Soc.* **1979**, *101*, 3971–3973.

(32) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850–1851.

(33) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700–701.

(34) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333–4335.

Propagation:

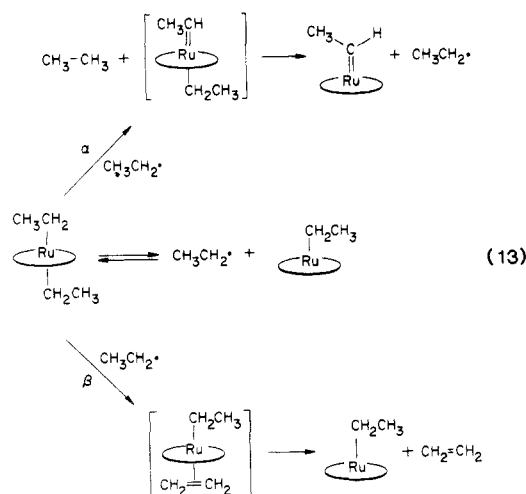


Related radical chain processes are probably involved in other apparent insertions into the Rh-H bond. For example, *n*-butyl isocyanide^{35a} and styrene³⁴ produce, respectively, formimidoyl- and (2-phenylethyl)rhodium(III) porphyrin derivatives. A variety of aldehydes undergo the insertion reaction under H₂ pressure.^{35b}

Attack of the rhodium dimer on the allylic position of olefins¹⁹ is doubtless another case where this mechanism prevails. The key is the abstraction of an allylic hydrogen by $\bullet\text{Rh}(\text{OEP})$. Similarly, oxidative-addition of a methyl C-H bond in toluene or xylene to produce the benzyl rhodium derivative and the rhodium hydride are yet other examples of these free-radical chain processes.³⁶

The radical chain mechanism outlined here is a remarkable advance in this field because it satisfactorily rationalizes a process (eq 8) hitherto considered to be thermodynamically unfavorable, and mechanistically notable because of the new pathway arising in the absence of a cis coordination site. This type of radical mechanism has even wider applicability. For example, solutions of the bis(ethyl)ruthenium porphyrin complex decompose first to a mixture of ethylidene and ethylene complexes, and finally to pure ethylene complex.^{1d,13} The rearrangement of bis(ethyl) to ethylidene is complete in hours at 30 °C.

A mechanistic study demonstrated that the conversion of ethyl to ethylidene ligands is also a radical chain reaction (eq 13). It was demonstrated by NMR that



the initial step is reversible homolysis of the ruthenium-carbon bond in the bis(ethyl) complex to produce the stable ruthenium(III) monoethyl species and a free ethyl radical which subsequently abstracts either an α or a β hydrogen from the initial bis(ethyl) complex (eq 13).¹³

Addition of an excess of a radical trap suppresses the formation of both the carbene and olefin complexes and results in a first-order decomposition of the bis(ethyl)

species.¹³ From the activation energy, the ruthenium-carbon bond energy was determined to be 22 kcal mol⁻¹. This surprisingly low value is undoubtedly due to the trans effect of the second ethyl group. Under these conditions Ru(OEP)(C₂H₅) is stable.

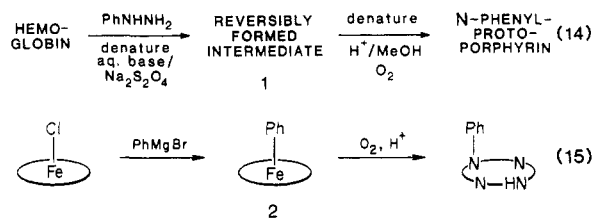
In contrast to the ruthenium diethyl complex, bond energies in rhodium alkyl and formyl derivatives are estimated to be much higher, in the range 50–60 kcal mol⁻¹;³⁶ crystal structures of Rh(OEP)(CH₃)³⁷ and Rh(OEP)(CHO)^{35a} manifest short, presumably strong Rh-C bonds. However, νCO in the formyl complex is unexpectedly high. The factors which influence these axial metal-carbon bond strengths in organometallic porphyrin compounds are not well-understood and are of great current interest.

These results are significant in demonstrating that classic organometallic processes such as α - and β -hydrogen elimination and CO insertion, when observed in the above metalloporphyrin systems, proceed via a radical mechanism. In classical organometallic chemistry all of these processes share the requirement of a vacant cis coordination site. It is interesting that in porphyrin complexes where cis sites are not readily available, similar transformations occur but by very different mechanisms.

Reversible Migrations between Metal and Pyrrolic Nitrogen

σ -Bonded Ligands. In certain instances, cytochrome P-450 mediates its own deactivation during the oxygenation of olefinic and acetylenic substrates. "Green pigments" isolated from the inactivated enzyme were shown to be N-alkylated heme groups. The treatment of erythrocytes, containing hemoglobin or myoglobin, with phenylhydrazine was also observed to produce green N-phenylporphyrins. A careful study of this latter case, for both biologically-derived and model iron porphyrin systems, has led to elucidation of a series of intermediates leading to the N-alkylated product, and has uncovered novel reactivity of organoiron porphyrin complexes.³⁸

Formation of the N-phenylprotoporphyrin IX (NPhPPIX) upon treatment of erythrocytes with phenylhydrazine was shown to proceed via a reversibly formed intermediate, 1, as in eq 14. This phenyl heme



complex 1 formed from phenylhydrazine-treated myoglobin was shown by ¹H NMR and electronic spectroscopy to be the same species as Fe(PPIX)Ph, 2, formed as in eq 15.³⁸ The N-phenylporphyrin is the result of an oxygen-dependent oxidative shift of the phenyl moiety of 1 from iron onto a pyrrolic nitrogen.^{38,39}

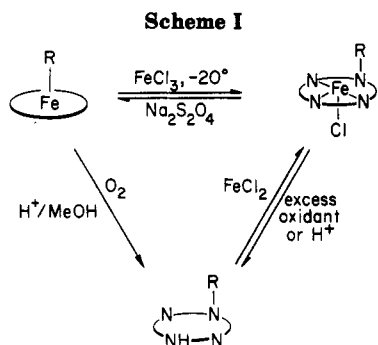
(37) Takenaka, A.; Syal, S. K.; Sasada, Y.; Omura, T.; Ogoshi, H.; Yoshida, Z.-I. *Acta Crystallogr. Sect. B Struct. Sci.* 1976, 32, 62–65.

(38) Kunze, K. L.; Ortiz de Montellano, P. R. *J. Am. Chem. Soc.* 1983, 105, 1380–1381, and references therein.

(39) Ortiz de Montellano, P. R.; Kunze, K. L.; Augusto, O. *J. Am. Chem. Soc.* 1982, 104, 3545–3546, and references therein.

(35) (a) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* 1982, 104, 302–303. (b) Van Voorhees, S. L.; Wayland, B. B. *Organometallics* 1985, 4, 1887–1888.

(36) Del Rossi, K. J.; Wayland, B. B. *J. Am. Chem. Soc.* 1985, 107, 7941–7944.



These results establish, then, that the reaction of hemoglobin or myoglobin with phenylhydrazine results in the formation of an iron-carbon σ -bond, and that the phenyl moiety then undergoes an oxidative shift to a pyrrolic nitrogen. This represents the first direct identification of a stable σ -bonded organoiron complex in a hemoprotein, and provides an important precedent for other enzymic systems.

Further studies on synthetic iron porphyrin systems have established the iron-to-nitrogen shift demonstrated in the above study to be general and reversible for a variety of groups. Chemical oxidation of the iron phenyl complex induces migration onto a pyrrolic nitrogen, to form an iron(III) N-substituted porphyrin complex. This species can be chemically reduced, inducing the reverse migration (N to Fe), or demetalated to yield the free base N-substituted porphyrin. These transformations are summarized in Scheme I.^{38,40}

The detailed mechanism of the reversible migration step was revealed by a spectroelectrochemical study of Fe(TPP)(Ph) and Fe(OEP)(Ph).¹⁸ Each process occurs by an ECE mechanism. An initial one-electron oxidation of Fe^{III}(Por)Ph is followed by migration of the phenyl moiety from Fe to N. Similarly, the reverse (N to Fe) migration is induced by a one-electron reduction of [Fe(N-PhPor)]⁺. Each species on the forward and reverse pathway was observed spectroscopically and, where possible, compared with an independently prepared sample.¹⁸

To summarize, the Fe-to-N migration can be regarded as an oxidatively induced reductive elimination of N-Ph from an iron(IV) center and the reverse process as a reductively induced oxidative addition of N-Ph to iron(I). The stoichiometry of the actual migration steps parallels those of the oxidative addition and reductive elimination processes familiar in organometallic chemistry.

Reversible migration of a wide range of ligands (alkyl, aryl, α -styryl) between cobalt and a pyrrolic nitrogen in cobalt porphyrin complexes indicates the generality of the migration process described above for iron porphyrins.⁴¹ One-electron chemical or electrochemical oxidation of organocobalt(III) species initiates the migration of the organic substituent from cobalt to nitrogen.^{5,41} Like the iron process, the reverse reaction is induced by electrochemical or chemical reduction of the cobalt N-alkylporphyrin.^{4b} Isotope labeling of both the porphyrin and the migrating group indicated that both migrations are intramolecular processes.⁴¹

(40) Mansuy, D.; Battioni, J.-P.; Dupré, D.; Sartori, E. *J. Am. Chem. Soc.* 1982, 104, 6159-6161.

(41) Callot, H. J.; Cromer, R. *Nouv. J. Chim.* 1984, 8, 765-770, and references therein.

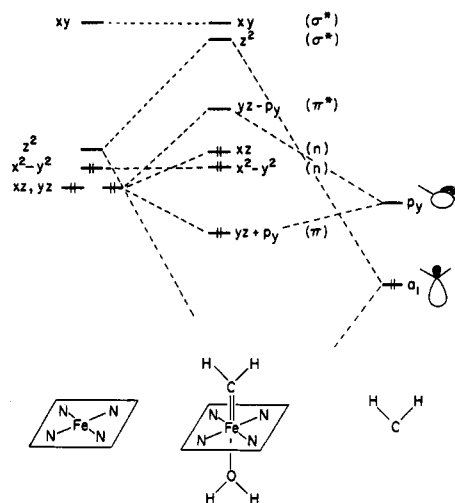


Figure 1. Energy-level diagram for a $\text{Fe}(\text{N}_4)(\text{CH}_2)(\text{OH}_2)^{2-}$ model.

π -Bonded Ligands. Two basic types of metalloporphyrin carbene complexes are found. First, the axially symmetric complexes 3 with multiple metal-carbon bond order are observed for iron and ruthenium. The unsymmetrical cobalt and nickel complexes [Co(OEP)(CHCO₂Et)]Cl⁴² and Ni(TPP)(CHCO₂Et)(OH₂)⁴³ contain the carbene fragment inserted into the metal-nitrogen bond as in 4. The relationship between the



two structural types has been addressed in a theoretical study⁴⁴ and will be discussed here.

The structural parameters from Fe(TPP)(CCl₂)(OH₂)²² were used in conjunction with models Fe(Por)(CH₂)(OH₂) and the simplified Fe(N₄)(CH₂)(OH₂)²⁻ to calculate an energy level diagram for the valence orbitals.⁴⁴ The results are quantitatively similar for both models and are shown for the latter, simpler model in Figure 1. Note that the CH₂ and OH₂ ligands are eclipsed to each other and staggered with respect to the four nitrogens of the porphyrin plane.

In a d⁶ system such as the iron structure, the σ , π , and two nonbonding levels are filled to give a net double bond between iron and the carbene. Substitution of nickel(II) for iron(II) in this scheme requires the addition of two electrons which would fill the π^* level and consequently disrupt the π -bonding. The bridging structure of the d⁸ nickel complex Ni(TPP)(CHCO₂Et)(OH₂)⁴³ is rationalized by this argument. However, both Fe(TPP)(CCl₂)(OH₂)²² and [Co(OEP)(CHCO₂Et)]Cl⁴² are d⁶ complexes, yet the former has the structure 3 while the latter assumes the bridged form 4, indicating that the MO description is inadequate, and some more subtle factors are involved in the structural preferences of these species. Further calculations indicated that for a given dⁿ, lowering the d orbital energy (which decreases in the order Fe, Co, Ni)

(42) (a) Batten, P.; Hamilton, A.; Johnson, A. W.; Shelton, G.; Ward, D. *J. Chem. Soc., Chem. Commun.* 1974, 550-551. (b) Johnson, A. W.; Ward, D.; Batten, P.; Hamilton, A. L.; Shelton, G.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* 1975, 2076-2085.

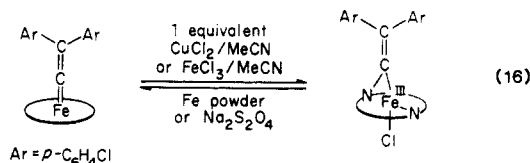
(43) Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* 1976, 98, 2985-2990, and references therein.

(44) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* 1981, 20, 3771-3784.

increases the relative stability of the bridged structure 4 over the symmetrical form 3.⁴⁴ Thus, both the low d orbital energy and d⁸ configuration of the nickel complex favor the bridged structure, but on going from an iron to a cobalt complex the decrease in d orbital energy is sufficient to favor structure 4 over 3.

Now, armed with a theoretical description of the bonding in the two types of carbene structure, it is of interest to see how further perturbations (for example, changing metals or changing the configuration of a given metal by oxidation or reduction) will affect the preference for each structure.

The reversible one-electron oxidation of the vinylidene complex Fe(TPP)(C=CAr₂) induces the carbene ligand to adopt a bridging structure (eq 16).^{45,46} Two



independent crystal structure determinations^{46,47} of the bridged species demonstrate it to be a severely distorted five-coordinate structure. The nitrogen involved with the bridging carbene is not bonded to iron (Fe-N 2.52 Å). The complex contains an intermediate spin ($S = 3/2$) iron(III) center.⁴⁸

On the simplest level, this process is analogous to the migration of σ -bound ligands. The one-electron oxidation of the vinylidene has induced migration of just one of the iron-carbon bonds to a pyrrolic nitrogen. Further oxidation causes the second bond to migrate, resulting in a *N,N'*-vinylidene-bridged porphyrin.

An analysis of this reaction within the framework of the MO description of metalloporphyrin-carbene bonding (Figure 1) shows that the electron removed from iron by oxidation of the vinylidene complex should come from a nonbonding orbital and should not disrupt the iron-carbene bonding. Some lowering of the d orbital energies on oxidation (as seen for cobalt and rhodium porphyrin complexes)⁴⁹ may account for the destabilization of structure 3. However, the energy level diagram calculated from the Fe(Por)(CH₂)(OH₂) model showed filled porphyrin π -orbitals with similar energy to the filled, nonbonding xz and $x^2 - y^2$ levels.⁴⁴ If, upon oxidation of Fe(TPP)(C=CAr₂), an electron was removed not from the d levels but from a porphyrin π -orbital, then the porphyrin ring would bear a positive charge, and the bridging structure might result from electrophilic attack of a pyrrolic nitrogen on the vinylidene carbon. The charge on this carbon atom was calculated to be negative,⁴⁴ which is in accord with this proposal. In contrast, the carbon of the Fe=CCl₂ fragment was calculated to be highly positively charged.⁴⁴ If this mechanism has some validity, then this might explain why a bridging iron dichlorocarbene complex has not been reported.

(45) Wisniewski, T. J.; Gold, A.; Evans, S. A., Jr. *J. Am. Chem. Soc.* 1981, 103, 5616-5618.

(46) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J.-C.; Mansuy, D. *J. Am. Chem. Soc.* 1981, 103, 2899-2901, and references therein.

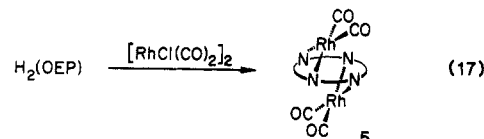
(47) Latos-Grazynski, L.; Cheng, R.-J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* 1981, 103, 4270-4272.

(48) Mansuy, D.; Morgenstern-Badarau, I.; Lange, M.; Gans, P. *Inorg. Chem.* 1982, 21, 1427-1430.

(49) Antipas, A.; Gouterman, M. *J. Am. Chem. Soc.* 1983, 105, 4896-4901.

Out-of-Plane Complexes

Among the more novel metalloporphyrin species are the "out-of-plane" or "sitting-atop" porphyrin complexes.⁵⁰ These contain a metal atom bonded to some or all of the pyrrolic nitrogens, but lying significantly out of the 4N equatorial plane. More than one metal may be coordinated to a single porphyrin. These species have been the subject of a theoretical study.⁴⁴ Treatment of H₂OEP with [RhCl(CO)₂]₂ under nitrogen at ambient temperature results in the rhodium out-of-plane species 5 (eq 17).^{4a,51} An X-ray crystal

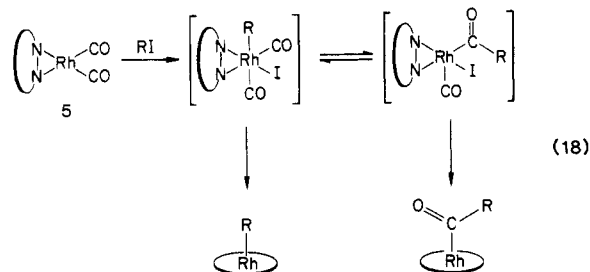


structure determination^{51a} shows that complex 5 contains two Rh^I(CO)₂ fragments, each coordinated to two pyrrolic nitrogens such that one rhodium lies above and the other below the porphyrin plane.

The dinuclear species 5 is air-oxidized in refluxing chloroform, resulting in collapse of one rhodium into the porphyrin plane to form a rhodium(III) porphyrin.^{51a} Organic substrates such as acid anhydrides, alkyl halides, and aldehydes react with 5 to form mixtures of alkyl and acyl products.^{51b,52} The reaction of 5 with iodine in CHCl₃ at ambient temperature to produce the rhodium(III) iodide complex is a useful entry into rhodium porphyrin chemistry.⁵²

The remarkable range of reactivity of 5 is further illustrated by reactions involving the opening of cyclopropane to form γ -substituted alkyl derivatives and the activation of C-H bonds of methyl ketones yielding α -keto methyl complexes.^{51b}

The reaction of these various organic substrates with the Rh^I complex 5 are formally oxidative additions. A general scheme proposed for these processes begins with oxidative addition of R-X (C-H, RCO-H, H-OAc, I-I, etc.) to the square-planar Rh(CO)₂(*N*-pyrrole)₂ fragment, forming a six-coordinate intermediate. Collapse of rhodium into the 4N equatorial plane may occur either before or after migration of R onto a CO ligand, to form the alkyl or acyl species, respectively (eq 18).^{51b,53}



Formation of an out-of-plane metal complex, followed by oxidative collapse into the macrocyclic plane may be a general mechanism for the insertion of some

(50) Lavalley, D. K. *Coord. Chem. Rev.* 1985, 61, 55-96.

(51) (a) Takenaka, A.; Sasada, Y.; Ogoshi, H.; Omura, T.; Yoshida, Z.-I. *Acta Crystallogr. Sect. B Struct. Sci.* 1975, 31, 1-6. (b) Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *Tetrahedron Lett.* 1976, 289-292.

(52) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans. 1* 1977, 1395-1403, and references therein.

(53) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; King, T. J. *J. Chem. Soc., Perkin Trans. 1* 1979, 2184-2192.

transition metals into porphyrin ligands. This may be especially true for ruthenium, osmium, rhenium, and other species where the metal is derived from a polycarbonyl complex and may insert as a $MCl_x(CO)_y$ fragment. Out-of-plane complexes are also known for rhenium⁴⁴ and iridium.^{4c}

Summary

The breadth of structural species discussed here represents the scope of organometallic chemistry quite well, with examples of metal-carbon single and double bonds, π -complexes, and hydride species. Notably absent are metal-carbon triple bonds (carbynes), π -allyl ligands, and many electron donor ligands such as η^5 - C_5H_5 and η^6 - C_6H_6 . The latter two may not be possible as ligands except for severely distorted, out-of-plane geometries of the metalloporphyrin fragment, but the former two may become accessible by new synthetic approaches.

Many of the traditional reactions of organometallic chemistry are also exemplified by porphyrin-containing species. Oxidative addition and reductive elimination are observed in the guise of the reversible, redox-induced metal-to-nitrogen migrations in cobalt and iron species. Ligand rearrangements, and a bimolecular coupling process are observed for several ruthenium complexes. Although the mechanisms of all of these have not been elucidated, the steric requirements of the porphyrin indicate that they may be interesting. In the instance of the insertion reactions involving the rhodium hydride and dimeric rhodium species, mechanisms new to both porphyrin chemistry and organometallic chemistry have been identified.

The porphyrin ligand itself has become involved in the context of both structure and reactivity, the former in the bridging carbene species and the latter in the

metal-to-nitrogen migrations.

The validity of organometallic porphyrin complexes as models for biological systems was demonstrated in the elegant study on σ -aryl migration from iron to pyrrolic nitrogen. This may also be involved in cytochrome P-450 chemistry.

Much of the material discussed was approached from the standpoint of synthetic and structural organometallic chemistry. The detailed electrochemical investigations of several iron complexes were very helpful in understanding both the properties and reactivity of these systems. Further mechanistic studies and X-ray crystal structure determinations would be useful.

The chemistry described in this account has been limited to the iron and cobalt triads, with single examples of nickel and molybdenum species. Alkyl complexes of main-group porphyrins are also known for gallium, indium, germanium, and tin.⁵⁴ As synthetic limitations are overcome, the entire range of metalloporphyrins will undoubtedly exhibit an organometallic chemistry. The connections between organometallic porphyrin chemistry and biological transformations should become more significant.

The support of the National Science Foundation (CHE83018512), the National Institutes of Health (GM17880-13,14), the CNRS (Centre Nationale de la Recherche Scientifique, France) and NATO (North Atlantic Treaty Organization) are gratefully acknowledged. We would also like to thank Steven Frank (for synthetic work), Dr. Lisa McElwee-White and Gregory Venburg (for helpful discussions), and Dr. Eric Rose (Univ. Pierre et Marie Curie, Paris VI, Laboratoire de Chimie Organique, Tour 44-45-4, Place Jussieu, 75230 Paris Cedex).

(54) (a) Coutsolelos, A.; Guillard, R. *J. Organomet. Chem.* 1983, 253, 273-282, and references therein. (b) Cloutour, C.; Lafargue, D.; Richards, J. A.; Pommier, J.-C. *J. Organomet. Chem.* 1977, 137, 157-163, and references therein. (c) Maskasky, J. E.; Kenney, M. E. *J. Am. Chem. Soc.* 1973, 95, 1443-1448, and references therein.